NISTIR 89-4093

Executive Summary for the Workshop on Developing a Predictive Capability for CO Formation in Fires

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INTRODUCTION

This report summarizes the proceedings and findings of a <u>Workshop on Developing a Predictive Capability for CO Formation in Fires</u> which took place at the Surfside Holiday Inn, Clearwater Beach, Florida on December 3-4, 1988. This workshop was organized by the author of this report who serves as the leader for the priority project on Carbon Monoxide Prediction of the Center for Fire Research. The workshop was designed to provide input for a comprehensive research plan which is being developed for this priority research area.

The workshop was organized with several specific goals in mind. The first was to review the current understanding with regard to the amount of carbon monoxide (CO) produced in actual fires and the physical mechanisms by which high concentrations of CO can be generated. A second goal was to identify current intramural and extramural (grant) research projects of the Center for Fire Research (CFR) which are relevant to this priority research area. The third, and perhaps most important, goal was to make recommendations concerning the research required to address this priority area. The recommendations contained in this report are based on a consensus of the participants in the workshop.

The scientists chosen to participate in the workshop are experts in the fields of combustion and fire science. An early decision was made to limit the number of participants to roughly fifteen even though it was recognized that some important researchers in the area would be excluded. This decision was made to assure a manageable meeting and to allow for active participation by all. In practice, a core group of invitees was joined by several other researchers at various times during the workshop.

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Appendix A is a list of the workshop attendees as well as others who took part at various times. A couple of notes are appropriate. Professor Ed Zukoski of the California Institute of Technology was scheduled to attend the workshop, but was forced to withdraw at the last minute due to illness. Dr. Quintiere of CFR agreed to make a presentation of the recent research findings of Professor Zukoski's group. Several members of the staff of Factory Mutual Research Corporation were invited, but were unable to attend due to scheduling conflicts.

The schedule for the workshop was designed to achieve the goals listed above and is included as Appendix B. With minor revisions, this schedule was adhered to. Following an introduction by the chairman of the workshop, short presentations of recent research activities were made by several participants. These were designed to provide a flavor for current research relevant to the priority project and to form a foundation for later workshop deliberations. The talks were roughly ordered so that fundamental studies were presented first with the more applied engineering studies following. The chairman then presented a short recap of the morning session and an introduction to the working group session which was to follow.

Following an afternoon break, the workshop reconvened in the late afternoon. The participants were broken into two working groups constituted to deal with "fundamental" (group I) and "engineering" (group II) aspects of the workshop topic. Professor Gerard Faeth of the University of Michigan chaired the fundamental group and Dr. Craig Beyler of Fire Science Technologies chaired the engineering group. Appendix C contains lists of members of the two working groups and Appendix D is the written instructions provided to group members. As Appendix D indicates, the two working groups were to identify major issues and make recommendations for the research

required to address these issues. Each group was requested to provide a written summary of their findings and to prepare for short presentations of their conclusions the following day. The working group meetings were quite lively and informative and each group was able to generate the required outputs.

The following morning the workshop came together as a whole and the chairman of each working group made a presentation summarizing the deliberations of their group and provided recommendations of research areas which should be pursued. Each presentation was followed by wide-ranging discussions which served to clarify some points and further focus the findings of the two groups.

In the final session of the workshop a general consensus of all workshop participants was reached concerning the research which should be emphasized as a focus of the CO Formation Priority Project. A series of recommendations was formulated.

In the following sections of this report the individual presentations are briefly summarized, the deliberations and recommendations of the two working groups are discussed, and the final recommendations of the workshop participants are provided.

It should be noted that an earlier "Workshop on CO Formation in Fires" was organized by Dr. Robert Levine of CFR and took place in Philadelphia, PA on November 7, 1985. Many of the participants in the most recent workshop were also present at this earlier gathering. Even though the more recent workshop had different goals and was not intended to be an extension of the earlier meeting, it is of some interest to compare the findings of both. Appendix E is a list of research areas and their relative importance which were identified during the earlier workshop.

SUMMARY OF SHORT PRESENTATIONS

Presentations took place during the morning of the first day of the workshop. Each speaker provided a short summary of his talk prior to the meeting. These were distributed to the group. These summaries are grouped together in Appendix F. Note that Dr. Quintiere substituted for Professor Zukoski and discussed the ongoing work at Cal Tech.

This section includes summaries of the oral presentations of the speakers. Even though not formally part of the research review, the introductory remarks of William Pitts, workshop chairman, are also summarized.

<u>Dr. William M. Pitts</u>, Center for Fire Research, NIST

The physiological effects of CO on humans were reviewed briefly. Table 1 lists the concentrations required to induce various effects. Several examples of fire tests were shown which indicate that concentrations of CO in structures often reach extremely hazardous levels. Perhaps the most dramatic example is the Sharon, PA fire of September 26, 1987 where one of the victims was found to have a very high (certainly fatal) carboxyhemoglobin level.

The complexity involved with predicting CO levels in real fires was stressed by listing the stages in a real fire. From this list it was clear that the mechanisms responsible for CO formation would change during the history of an enclosure fire.

Two general approaches to the problem of predicting CO formation in fires, fundamental and engineering, were discussed. The speaker indicated the current level of understanding with regard to both strategies. It was clear that significant experimental research and theoretical development is required before CO levels in fires can be predicted with confidence.

Table 1

CO TOXICITY

- CO binds to hemoglobin to form carboxyhemoglobin

- CO binding affinity is 220 to 280 times higher than O_2

- Concentration of 2000-2500 ppm produces unconsciousness in 30 minutes

- Concentration of 4000 ppm is fatal in less than hour

- Concentration of 13,000 ppm results in unconsciousness and danger of death in one to three minutes

- Exposure to 50,000 ppm can result in fatal cardiac arrhythmia and death before carboxyhemoglobin saturation is significantly elevated

Professor J. Houston Miller, George Washington University

Two major topics were discussed. The first dealt with the partial equilibrium assumption which is often utilized to calculate free radical concentrations in laminar diffusion flames and the second applied the conclusions of this discussion to show that the use of global kinetic relationships for CO oxidation are unlikely to be accurate.

Experimental measurements of concentrations of stable species and the hydroxyl radical (OH) were discussed for a laminar methane/air diffusion flame stabilized on a Wolfhard-Parker slot burner. Measured CO concentrations within the flame were found to collapse to a single curve when plotted in terms of the local fuel equivalence ratio (ϕ).

Observed CO concentrations were shown to be very different than values predicted based on full chemical equilibrium. CO and other species are not in full equilibrium, but the collapse of CO as a function of ϕ indicates that CO is in partial equilibrium.

The following radical reactions were recently analyzed:

$H + O_2 = OH + O$ (R1)

$O + H_2 = OH + H$ (R2)

$OH + H_2 = H_2O + H$ (R3)

$2OH = H_2O + O$ (R4)

$CO + OH = CO_2 + H$ (R5)
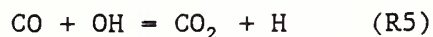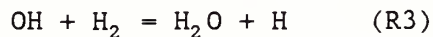
The analysis suggests that of the first three reactions, only (R3) is in partial equilibrium.

Global kinetic mechanisms for CO oxidation assume that the appropriate rate equation can be written as

$$-d[CO]/dt = k_{eff}[CO][O_2]^{\frac{1}{2}}[H_2O]^{\frac{1}{2}}.$$

In order for this relationship to hold reactions (R2) and (R3) must be in partial equilibrium and (R5) is assumed irreversible. Their work shows that this is not true in a methane/air diffusion flame. On this basis, global reaction mechanisms are not expected to provide accurate predictions of CO.

Support for this conclusion was provided by comparing the predicted concentrations of CO utilizing three global kinetic expressions available in the literature with experimental measurements. Figure 1 shows a plot of the results. It is clear that the global expressions provide a wide range of predictions all of which are in disagreement with experimental findings, thus confirming the hypothesis that the use of a global kinetics expression for CO oxidation is inappropriate for this flame.

Professor Robert Santoro, The Pennsylvania State University

Professor Santoro's primary research interest has been the formation and destruction processes for soot in hydrocarbon diffusion flames. He pointed out that in most past studies the role of soot in flame chemistry has been ignored despite the experimental findings that 20 - 30% of carbon for a typical fuel passes through soot. The oxidation of both soot and CO are due primarily to the OH radical so it is possible that the amounts of each of these products of incomplete combustion released by a flame will be dependent on their relative concentrations and reactivities within the flame. Additionally, the oxidation of soot may provide an alternate source of CO. Flame temperatures are expected to be very important since both formation and destruction processes are highly temperature sensitive.

A research program designed to investigate the correlation of soot and CO concentrations has been initiated. Experiments are to be made immediately above and within a laminar diffusion flame of methane with small amounts of
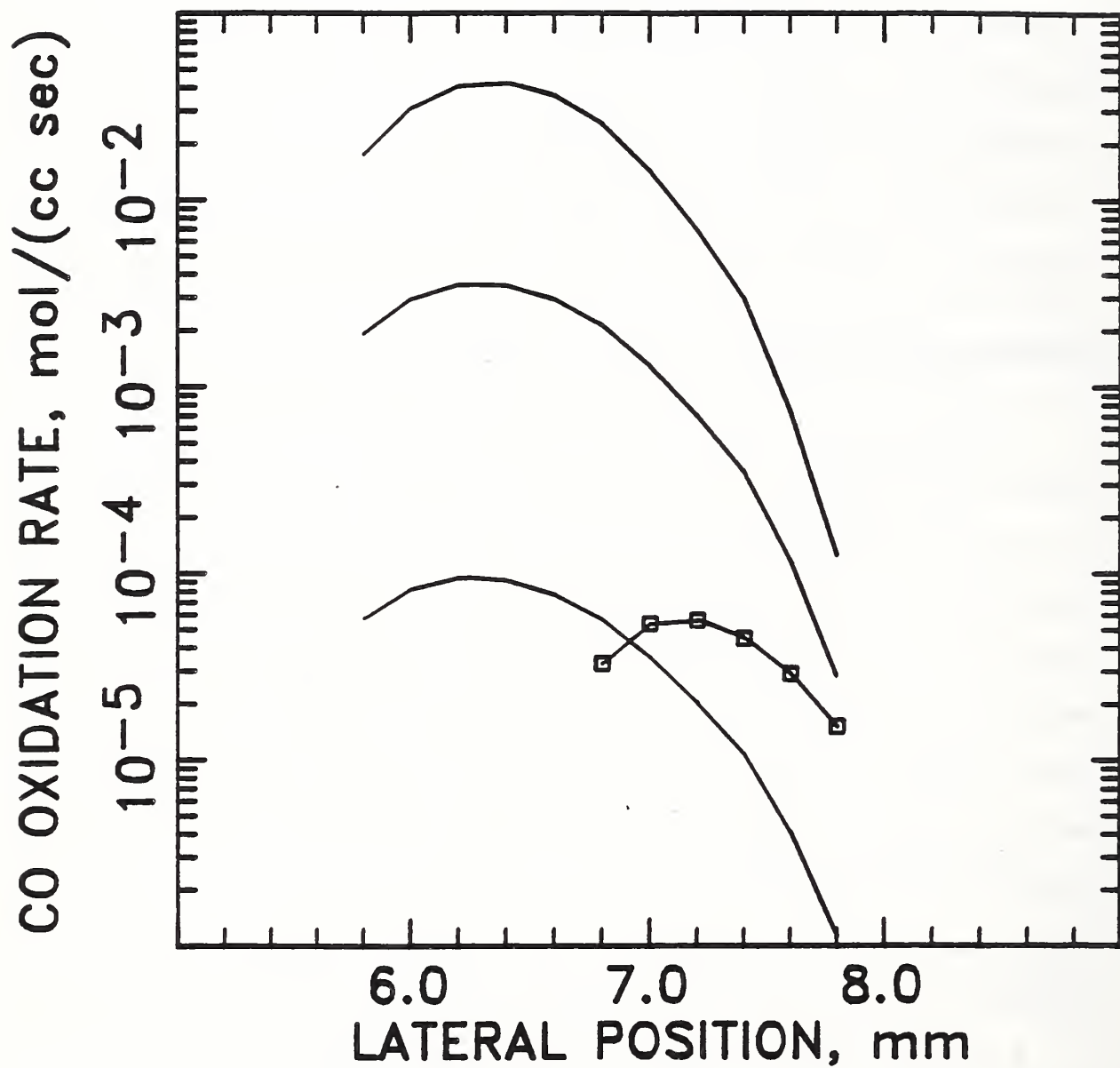
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Figure 1

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other fuels added. The behavior of the soot number density and volume fractions has already been characterized for butadiene, butene, and butane added to methane. Measurements of CO in the same regions of these flames have just begun.

One of the most difficult problems to be overcome is the need to measure CO concentrations in regions where high soot concentrations exist. Early measurements showed that a probe with a 0.7 mm orifice was clogged in three seconds when placed in a butadiene flame. In order to overcome this problem, the tip of the probe has been charged to a high voltage. This method is based on earlier work of Bonczyk and Sangiovanni (Combustion Science and Technology 36 (1984) 135) which showed that a high positive voltage prevented soot from entering a sampling tube. Very preliminary experiments in the region above a butadiene flame indicate that this new probe can sample for long periods of time without clogging. Figure 2 shows examples of early measurements made as a function of radial position above a baseline methane flame and a flame where a small amount of ethylene has been added to the methane fuel.

It is hoped that the experiments will allow the following questions to be answered:

1. Does soot appear in sufficient quantities to compete with CO for oxidizing species?

2. Is it possible to systematically vary soot concentration and investigate question 1?

3. What are the relative importance of temperature effects on the formation and oxidation processes?

Dr. Richard Yetter, Princeton University

An overview of research efforts at Princeton dealing with the oxidation of CO was presented. Four major research areas were mentioned.
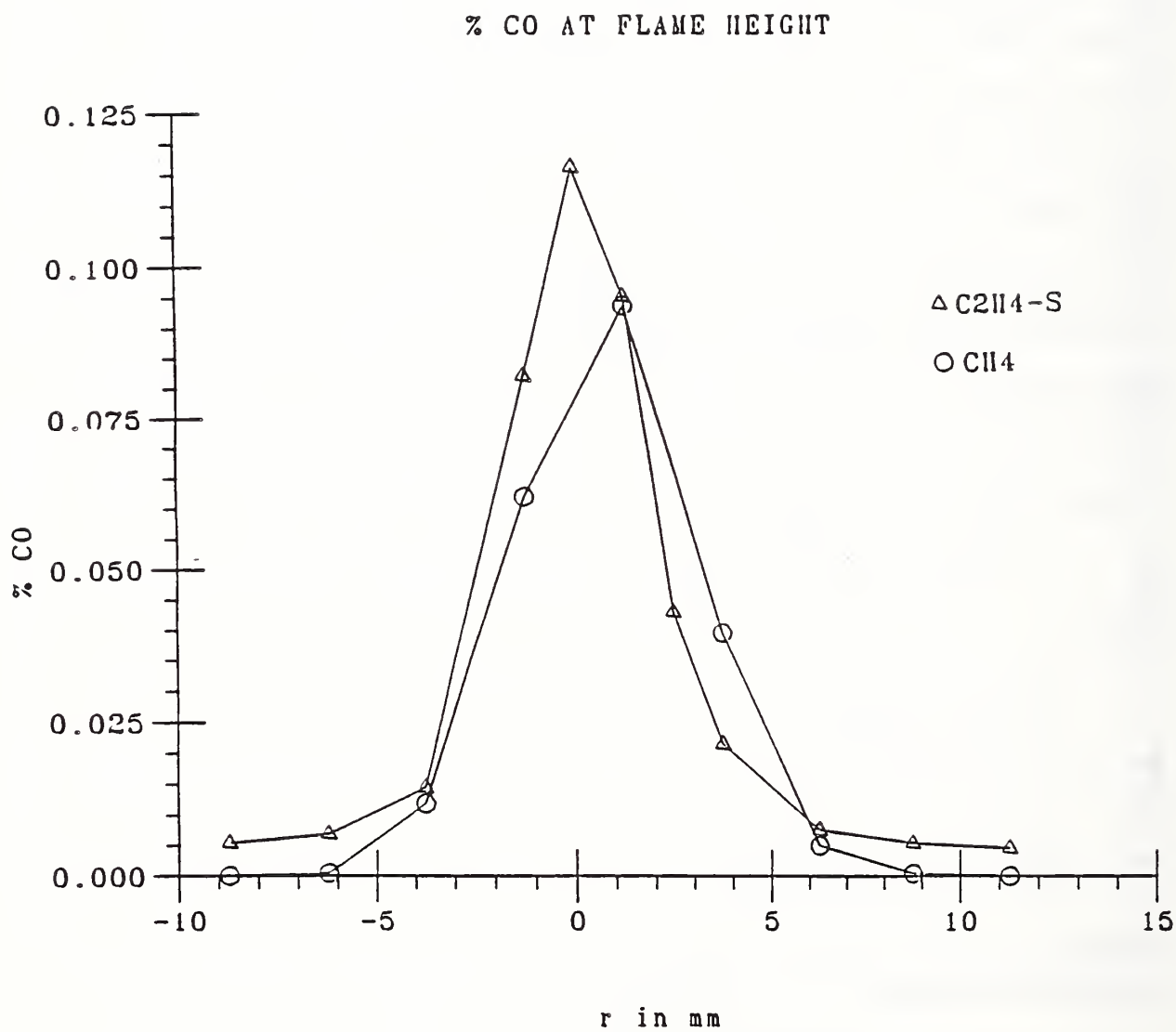
% CO AT FLAME HEIGHT

Figure 2

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The first area deals with the full kinetic modeling of the $CO/H_2/O_2$ system. The model has been found to provide accurate predictions of major species for a temperature range of 800 to 3000 K, a pressure range of 0.3 to 3 atmospheres, and an equivalence ratio range of 0.001 to 6.0. This work has shown that an earlier estimate for the rate constant of the important

$$H + O_2 \rightarrow OH + O$$

reaction is incorrect for temperatures above 2000 K. A very recent measurement by Pirraglia et al. provides much-improved agreement of modeling results with experimental findings.

The second area involves the changes in reaction mechanism which occur when nitrogen oxides are added to the reaction system. Model calculations have shown that small amounts of NO are sufficient to inhibit the oxidation of CO due to a reduction in H atom concentrations.

The third area concerns the use of CO reactions as diagnostics for investigating reaction pathways and measuring rate constants. The effects of adding small amounts of hydrocarbon or chlorinated hydrocarbons to the reaction system are being assessed. The importance of these measurements can be understood by considering Figure 3. Concentration and temperature profiles as a function of position are shown for hydrocarbon laminar premixed and diffusion flames. The hatched regions correspond to positions where the heat release and chemical reaction rates are highest. It can be seen that high concentrations of CO and CO_2 exist in these regions in the presence of lower concentrations of O_2 and hydrocarbons.

Experimental results indicate that small concentrations of hydrocarbons (< 1 %) can dramatically reduce the oxidation rate of CO. Sensitivity analysis allows the most important reactions to be identified. For added hydrocarbons, the most important reactions involve the CO system and OH attack

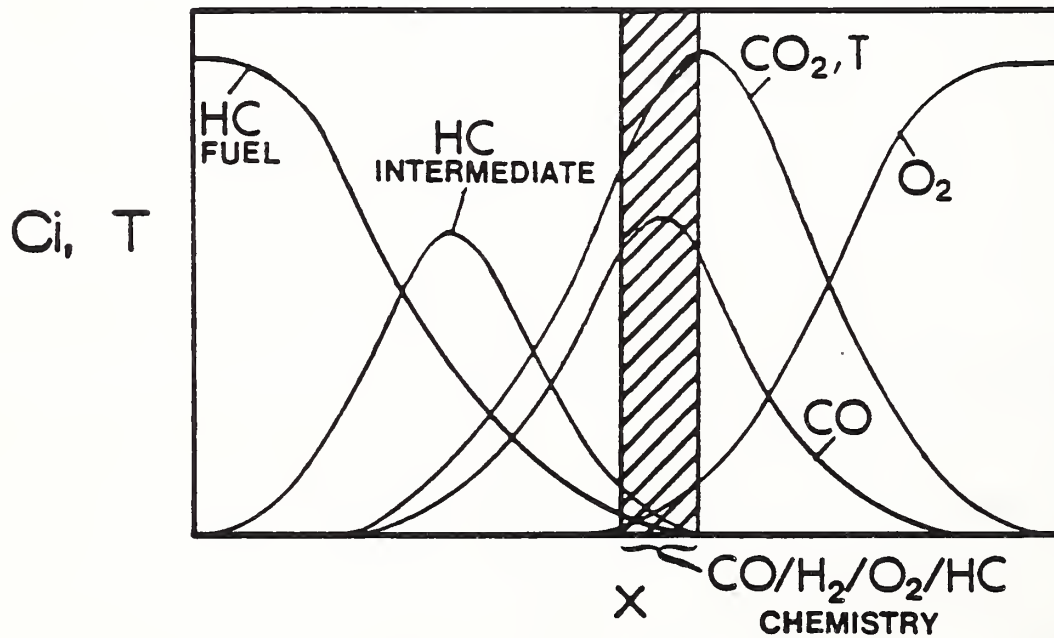# Laminar Premixed Flame
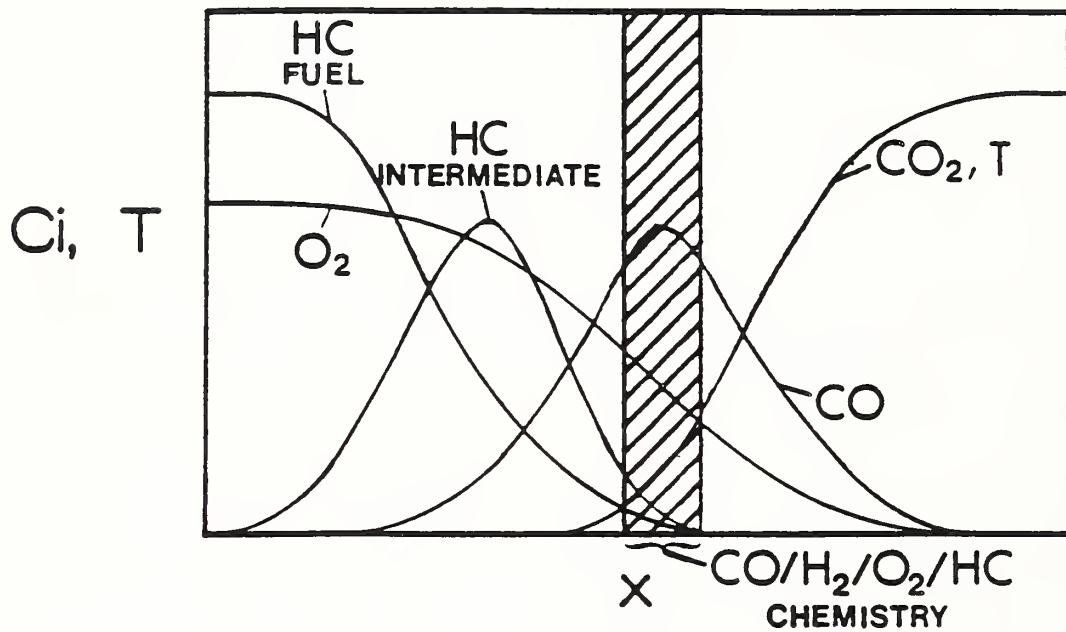
Laminar Diffusion Flame

Figure 3

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on the hydrocarbon species. Their analysis allows the reaction rate for the reaction of OH with the hydrocarbon species to be determined. Agreement with direct experimental measurements is excellent.

The fourth area was a discussion of global kinetics for CO oxidation. General rate expressions can be written as

$$-d[CO]/dt = k_{eff}[CO]^a[O_2]^b[H_2O]^c.$$

Comparisons of expressions found in the literature show that wide variations occur in suggested values of k_{eff} and even in the values of the coefficients. Detailed kinetic modeling indicates that these variations are to be expected and are due to variations in concentrations of the available free radical pool. Figure 4 compares the calculated reaction rate as a function of 1000K/T for a laminar premixed flame and an adiabatic flow reactor. The large differences are obvious. Its clear that a single global reaction cannot be used to describe both systems.

Brief mention was made of the various methods which are being used to generate reduced chemical mechanisms capable of accurate predictions of chemical behavior. The idea is to use an appropriately chosen short chemical mechanism to reproduce the results of a complicated full mechanism. This approach offers a possible means to reduce the time required for the computation of CO oxidation rates.

Dr. Vytenis Babrauskas, Center for Fire Research, NIST

Dr. Babrauskas' talk followed his outline included in Appendix F very closely. Only his major points are emphasized here.

CO remains the primary toxicant responsible for death in fires. This is true despite the wide-spread use of plastics which has occurred during the past thirty years. No "super-toxicant" appears to be released by these
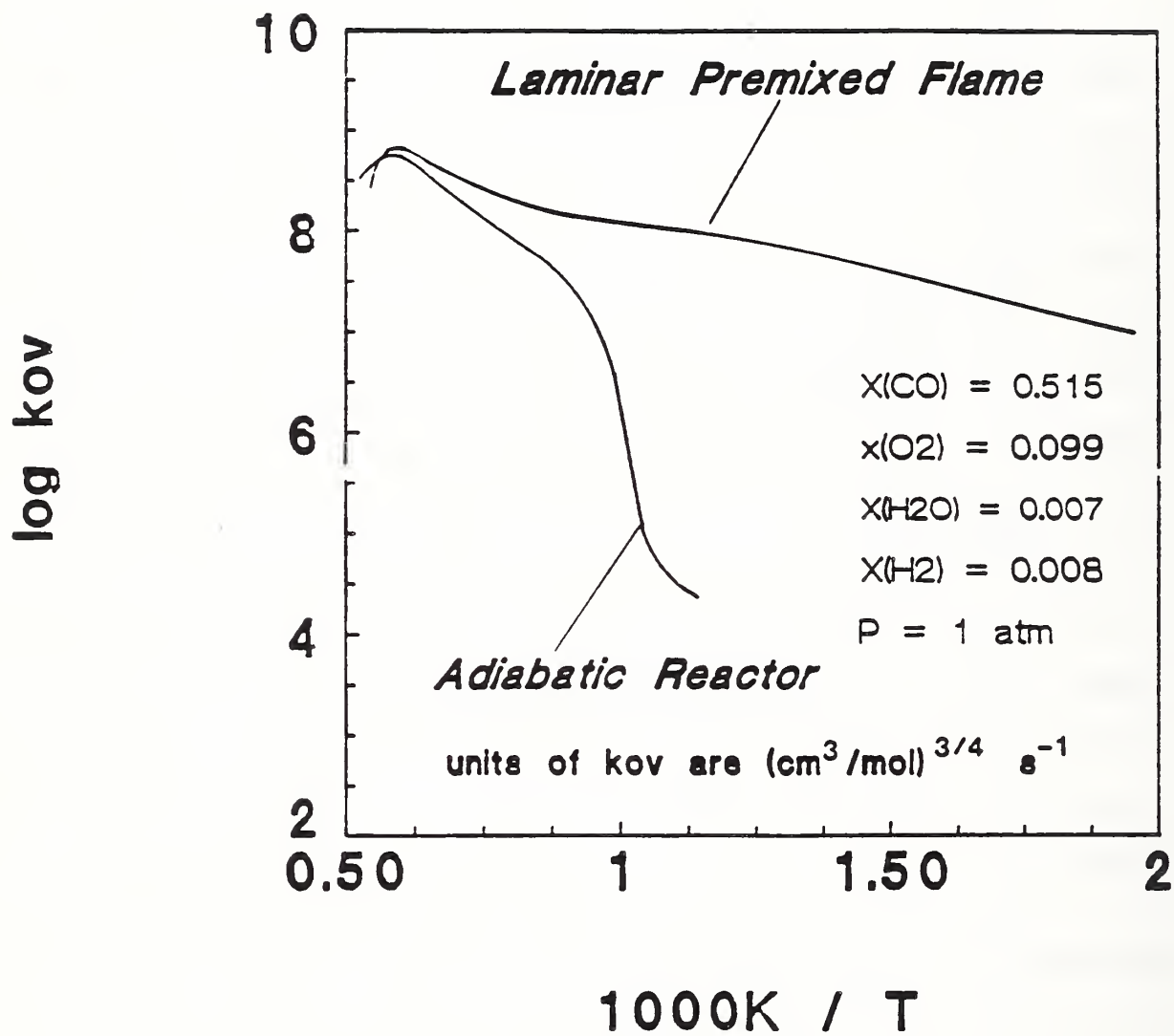
Figure 4

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materials. For this reason, prediction of CO concentrations from fires remains the most crucial need for assessing fire toxicity.

The important variable is the amount of CO released by a fire. This requires that the mass burning rate be known as well as the amount of CO produced per gram of fuel burned. Note that fire models are hampered by their inability to predict mass burning rate.

Studies have been performed to assess the effect of scale on the release of toxicants. The only toxicant for which scaling fails appears to be CO. Results from the cone and furniture calorimeters for CO production are not consistent with measurements in full-scale rooms.

A very important question concerns the effectiveness of the removal of CO by incineration in doorway plumes. A wide variety of observations has been recorded including cases where CO yields from postflashover fires are lower than in the preflashover case. These effects must be understood.

Experiments have indicated that CO yields might be correlated in terms of the global equivalence ratio. This should be checked for a wide range of conditions and scales.

Professor Gerard Faeth, University of Michigan

Professor Faeth's research program has been primarily concerned with radiation from combusting turbulent jets and plumes. It has been shown that the use of the laminar flamelet concept provides a useful framework for analyzing this complex problem. It is possible that the laminar flamelet concept can also be utilized to predict CO formation in similar combustion systems.

The laminar flamelet concept has its origins in the early work of Hottel et al. who assumed that a certain chemical state would be associated with the

degree of mixing in a combusting turbulent flow. In 1977 Bilger showed that state relationships for chemical species as functions of an appropriate conserved scalar (such as fuel equivalence ratio) are universal functions valid in both laminar and turbulent flames. This observation has led to widespread use of the laminar flamelet concept to treat turbulent combustion problems.

Examples of the state relationships for several fuel/air systems were shown and discussed. Figure 5 shows the experimental findings for various laminar methane/air diffusion flames. The collapse of data from a number of different experiments is quite good. Comparison of experimental findings with predictions based on full equilibrium suggest that flames are close to full equilibrium in the fuel-lean regions, but show departures from equilibrium on the fuel-rich side. No complete answer is available as to why universal curves are found in regions which are not in full chemical equilibrium.

Several potential problems were mentioned which might interfere with using the laminar flamelet concept to treat CO formation. When concentrations of a species are low (i.e., the species is a pollutant) the concept does not work. For instance, the laminar flamelet concept does not predict the low levels of CO emitted by a fully-ventilated fire. For turbulent jets with high stretch (high concentration gradients resulting from localized combustion and turbulent mixing) molecular diffusion times can become short enough to compete with chemical reaction times. This molecular diffusion can, in extreme cases, quench reactions which would otherwise react to completion. The laminar flamelet concept fails for this case. Fortunately, flame stretch values are relatively low and nearly constant in most buoyancy-driven turbulent flames.

Soot concentrations above turbulent flames have been found to obey state relationships when the flame residence time is sufficiently long. For short
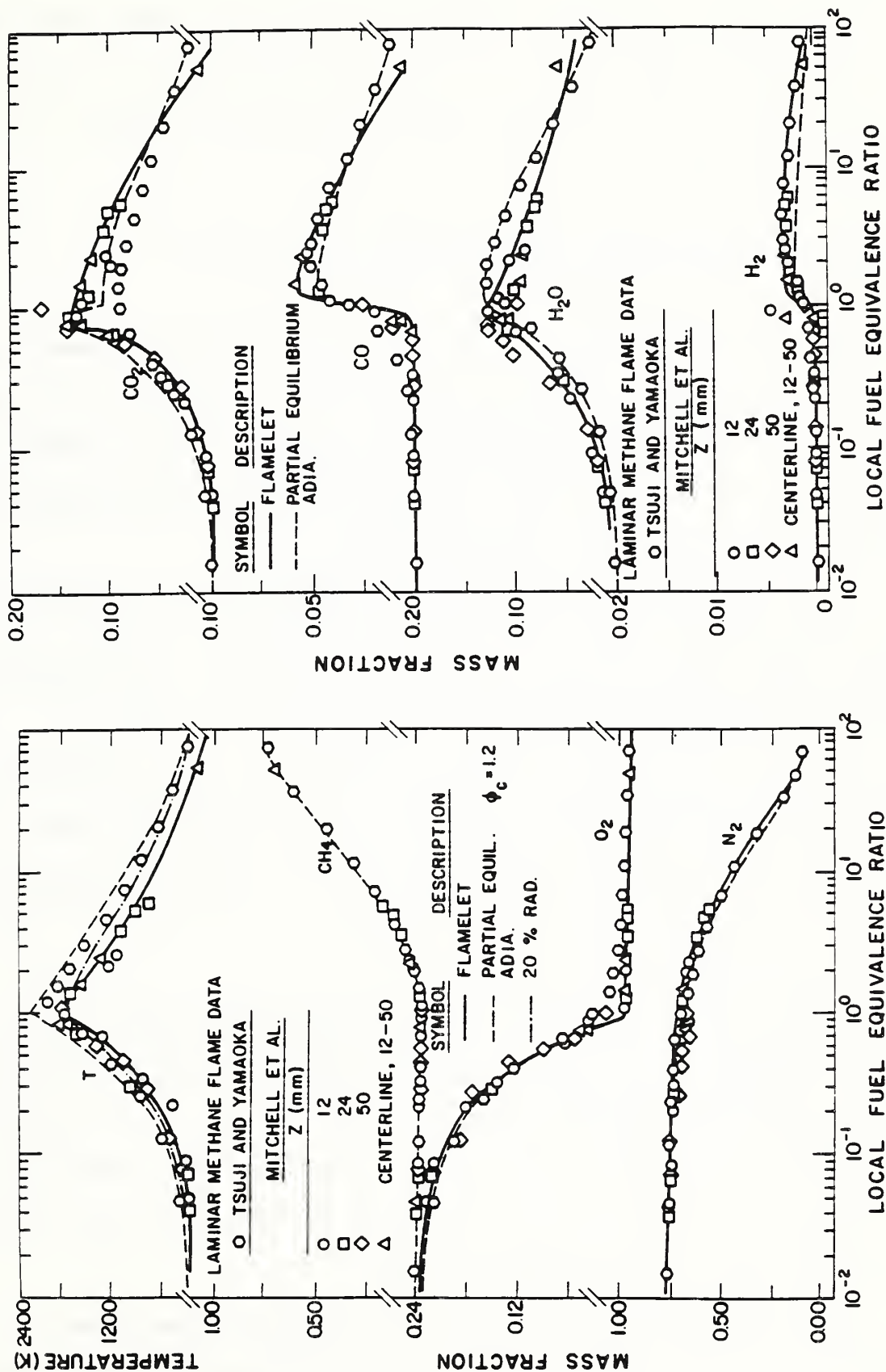
Laminar methane/air diffusion flames.

Figure 5

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residence times soot generation efficiency does not obey a state relationship. Results have been obtained for a range of fuels from acetylene to propane. It might be possible to use a similar analysis to predict CO releases, but this has not been tested.

Dr. James Quintiere, Center for Fire Research, NIST
(Discussing Professor Edward Zukoski's work at Cal Tech)

Professor Zukoski and his coworkers have been measuring the composition of the combustion products trapped in a well-mixed catcher-hood either above or completely surrounding a turbulent buoyant flame. This arrangement is much like the upper layer found in an enclosure fire. These experiments are extensions of earlier work by Cetegen and Toner.

Experimental measurements of mole fractions are correlated in terms of the global equivalence ratio in the layer. A new apparatus allows oxygen to be injected into the upper layer and thereby decrease the global stoichiometric ratio in the upper layer (denoted $\phi_{upper\ layer}$) from that determined by entrainment due to the turbulent plume (denoted ϕ_{plume}). This is intended to mimic the time dependent-behavior of an actual fire where a buoyancy-driven turbulent fire may enter an upper layer which has a high oxygen concentration.

Figure 6 shows the experimental results for the mole fraction of CO as a function of $\phi_{upper\ layer}$ where the air entrained by the plume below the layer is set to different values determined by ϕ_{plume}. The data all collapse onto a single curve. Note that the earlier data collected by Toner does not fall on the same curve. This is attributed to catalytic effects associated with the presence of fiber insulation on Toner's hood.

Similar measurements have been made with the fire plume submerged completely in the upper layer. As $\phi_{upper\ layer}$ increases the flame begins to
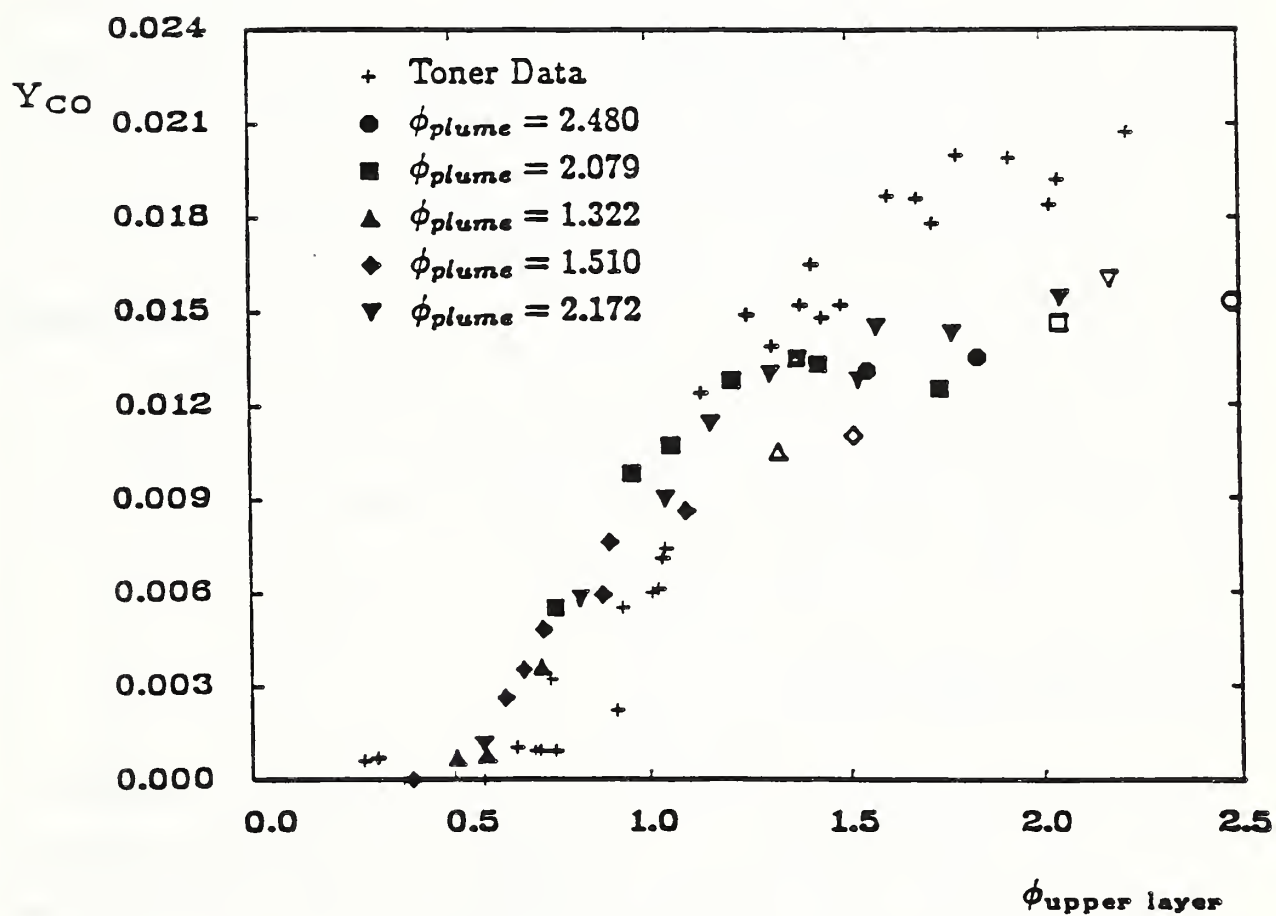
18

<u>Figure 6</u>

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turn blue (indicating a decrease in soot formation), but the heat output of
the fire remains relatively constant. Mole fractions of the principal flame
gases as functions of $\phi_{upper\ layer}$ are found to fall on the same universal
curves as measurements with an upper layer until the oxygen composition
becomes too low to support combustion. Extinction occurs when the oxygen mole
fraction falls in the range of 12-14% or $\phi_{upper\ layer} \approx 0.35$. For all of the
submerged jets, the concentrations of CO and H_2 are very low.

Orloff et al. (Factory Mutual Research Corporation Report RC85-BT-4,
August, 1985) have reported local time-averaged mass fraction measurements of
chemical species <u>within turbulent flames</u> as a function of time-averaged local
equivalence ratio. Figure 7 compares their measurements for O_2 and CO with
the Cal Tech measurements in the upper layer. It is clear that the two sets
of results are very different and that the FMRC results show more scatter. A
lively discussion of these findings took place on whether or not <u>time-averaged</u>
measurements within a combusting flow are expected to have a universal
behavior. The general consensus was that the answer is no, but since no
member of FMRC was present, the meeting chairman feels that this remains an
open question subject to later reinterpretation.

<u>Dr. Craig Beyler</u>, Fire Science Technologies
<u>Professor Richard Roby</u>, VPISU

These researchers have a joint grant from CFR. Dr. Beyler discussed an
analysis of the relative dangers of CO, oxygen depletion, and thermal hazards
for various fire conditions. Professor Roby described an experimental system
which is being constructed to study generation rates of major toxicants and
smoke in a realistic fire environment.

Figure 8 shows a plot of per cent O_2 depletion against ppm CO. The heavy
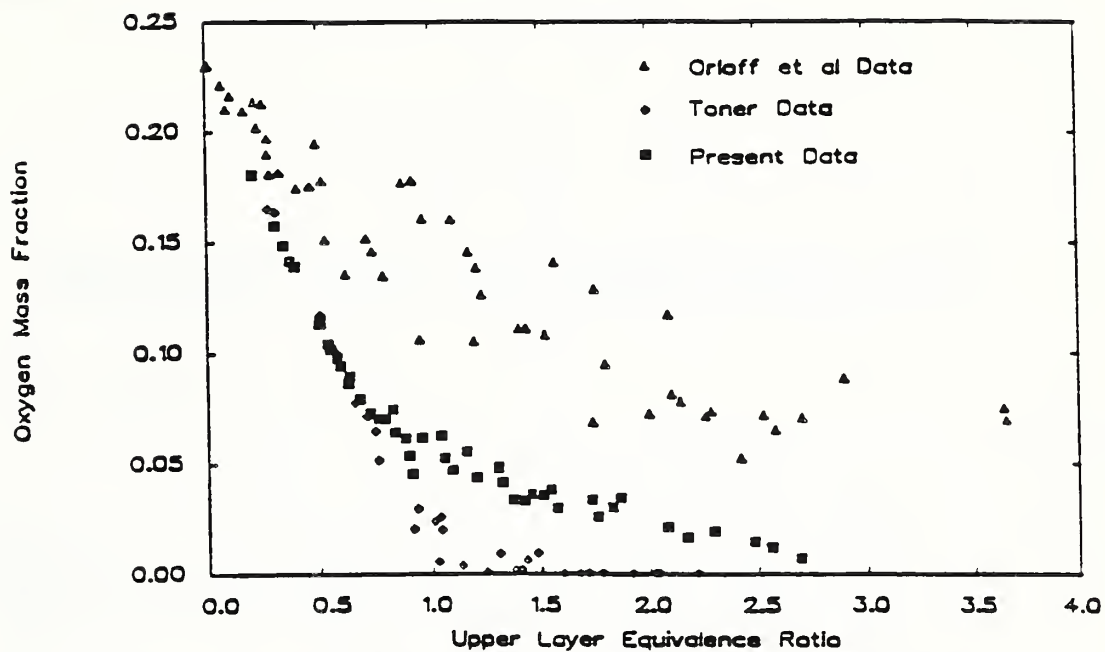dashed lines represent the values required to induce incapacitation or death

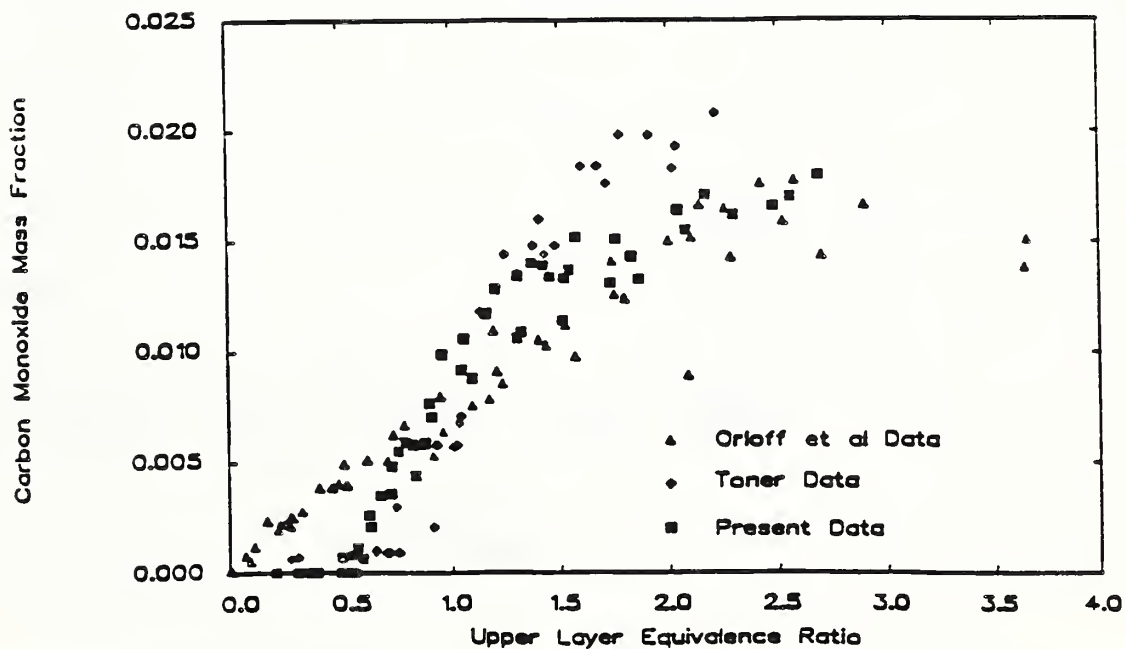Figure 1: Comparison of Oxygen Mass Fraction measurements

Figure 2: Comparison of Carbon Monoxide Mass Fraction measurements
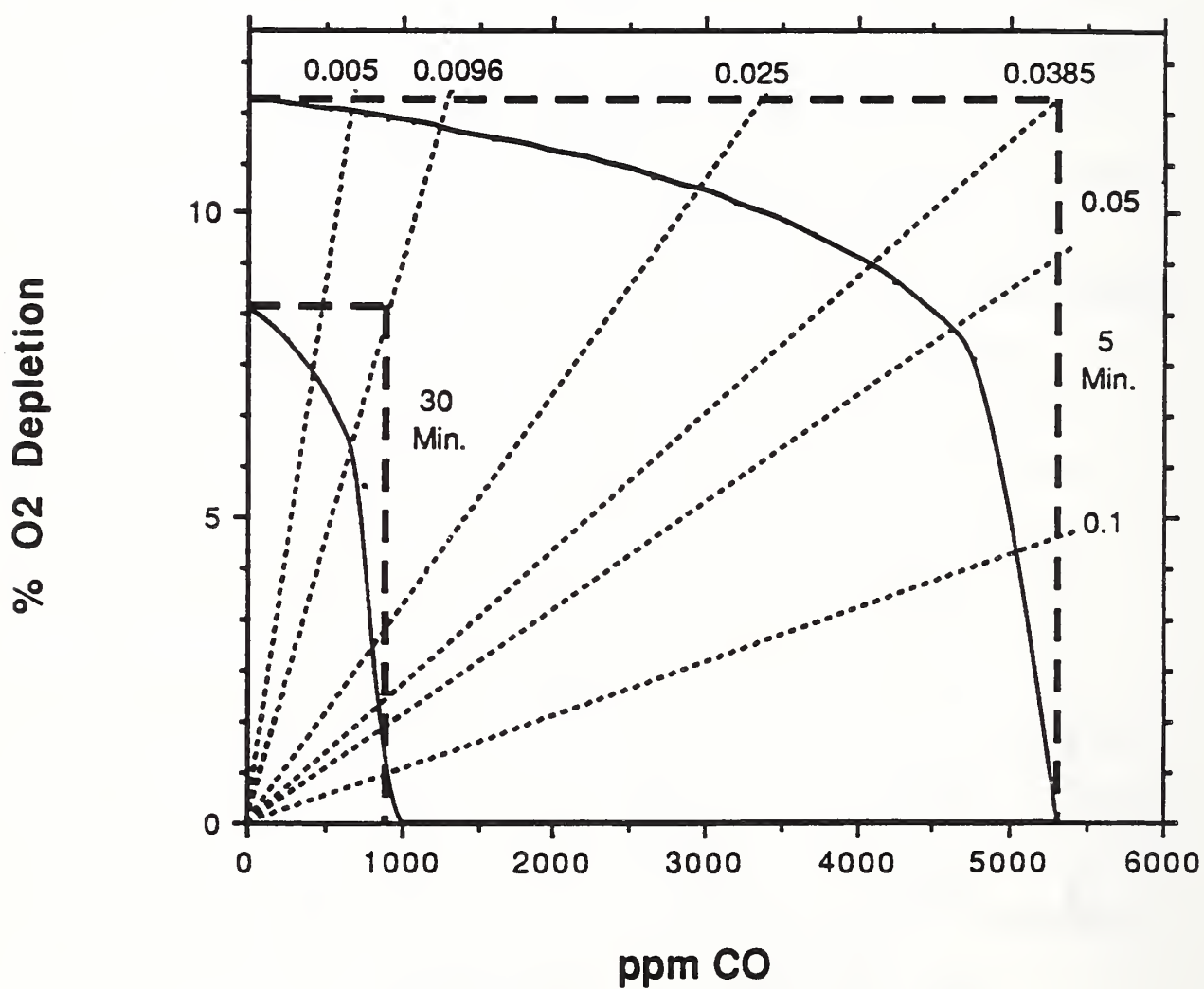
Figure 7

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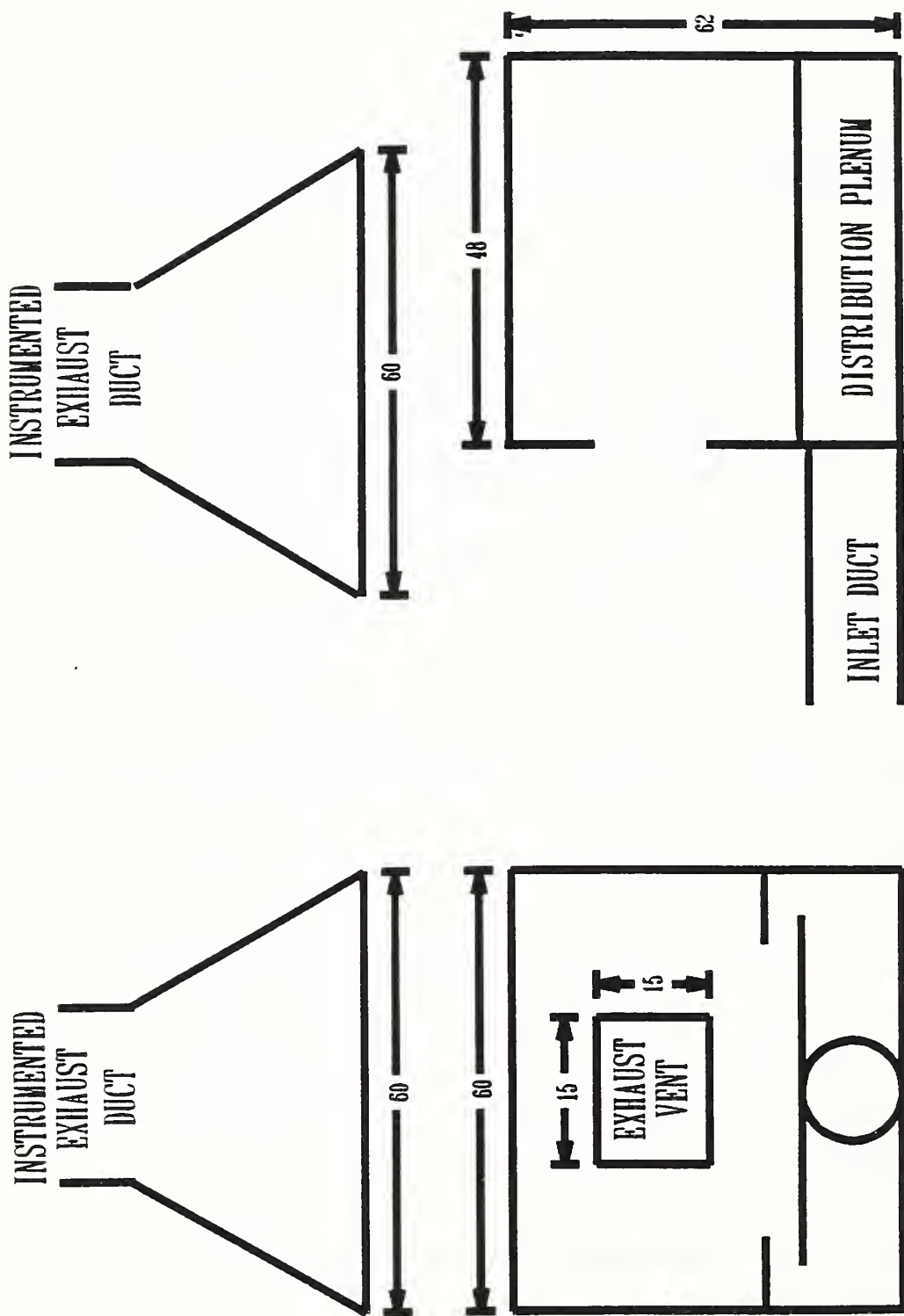# O₂ Depletion/CO Toxic Hazard

Figure 8

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in either five or thirty minutes. Normal breathing rates and the absence of other toxicants are assumed. The light dashed lines correspond to ratios of CO concentration and O_2 depletion. The most dangerous effect for a given time period and toxicant ratio is identified by the point where the light dashed line crosses the heavy dashed line. For short exposure times O_2 depletion tends to be the dominant effect, but as the exposure time is increased CO generally becomes more dangerous.

The available experimental data for O_2 depletion and CO formation in open burning, two-layer burning, and smoldering were analyzed to determine the dominant toxicant effect. For open burning, O_2 depletion and thermal effects represent the greatest danger. However, when the combustion occurs in the two-layer or smoldering modes the concentrations of CO are large and this toxicant becomes the most dangerous fire effect.

An experimental research program has been initiated at VPISU which has these three research goals:

1) Determine toxicant and smoke generation rates and their correlation with the global equivalence ratio for realistic compartment fire environments.

2) Determine major toxic species and smoke generation rates for important fuels including solids.

3) Determine the ability of an external flame to destroy toxicants produced in the compartment and vented through an opening.

Figure 9 shows two schematic views of the experimental system. The enclosure is roughly 1.3 meters on a side. The system is arranged such that controlled amounts of fresh air are introduced from the bottom of the enclosure and only products of combustion isolated in the upper layer exit from the exhaust vent. Measurements are to be made both within the enclosure and in the catcher hood.

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INSTRUMENTED EXHAUST DUCT

INSTRUMENTED EXHAUST DUCT

60

48

62

DISTRIBUTION PLENUM

INLET DUCT

EXHAUST VENT

15

15

60

60

FIRE COMPARTMENT SCHEMATIC

DIMENSIONS IN INCHES

Figure 9

Dr. George Mulholland, Center for Fire Research, NIST

The very simple two-level model for CO production shown in Figure 10 has been incorporated in the CFR hazard model. The suggested values of CO and CO_2 yields and CO/CO_2 ratio are based on the analysis of Dr. Mulholland of several full-scale burns in CFR over a period of years.

Very recently, a simulation was run at CFR of a townhouse fire in Sharon, PA which killed three people. It is believed that the fatalities were due to a combination of high temperatures, reduced oxygen levels, and high CO concentrations. The fire was located on the lower floor of the "townhouse" and measurements were recorded in two "bedrooms" situated upstairs. The test was run with a fuel loading sufficient to produce a 4 MW fire if burned in the open. After 130 seconds, a vent was opened in the burn room to simulate a window breaking.

Figure 11 shows the measured CO/CO_2 ratio as a function of time in the two upstairs bedrooms. In one bedroom the ratio approached the 0.5 value assumed in the simplified hazard model for a short period. However, on the average, the ratio is closer to that observed by Craig Beyler during his controlled two-layer burning experiments on Ponderosa pine. The lower CO/CO_2 ratio observed in this experiment, compared to earlier measurements at CFR, might be due to the increased ventilation resulting from breaking the window.

Measurements of the CO/CO_2 ratio were also made in the stack which collected the gases released through the vent in the fire room. Burning outside of the vent was observed. This was reflected in the measured ratios of CO/CO_2 which were significant, but reduced from those found in the upstairs bedrooms. This suggests that burning outside of the enclosure can significantly reduce CO emission.

PROPOSED CO YIELD MODEL

(For Application in Hazard Model)
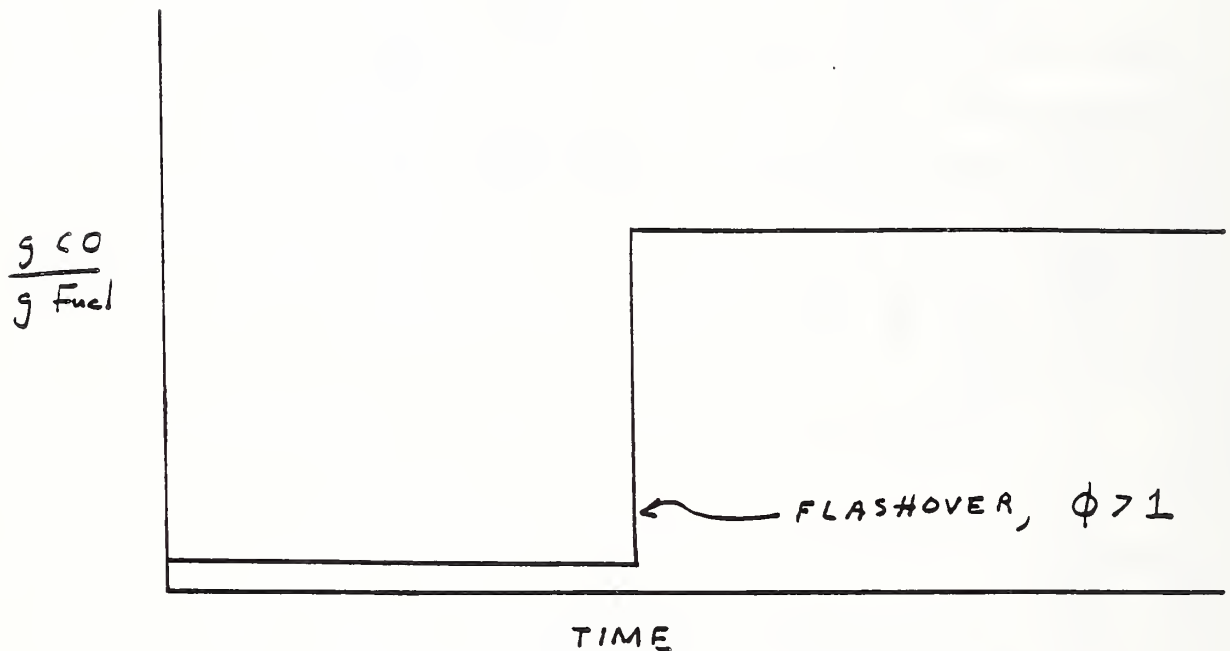
Example: Wood

PRE FLASHOVER - 0.002 g CO/g fuel burned

POST FLASHOVER - 0.3 g CO/g fuel burned
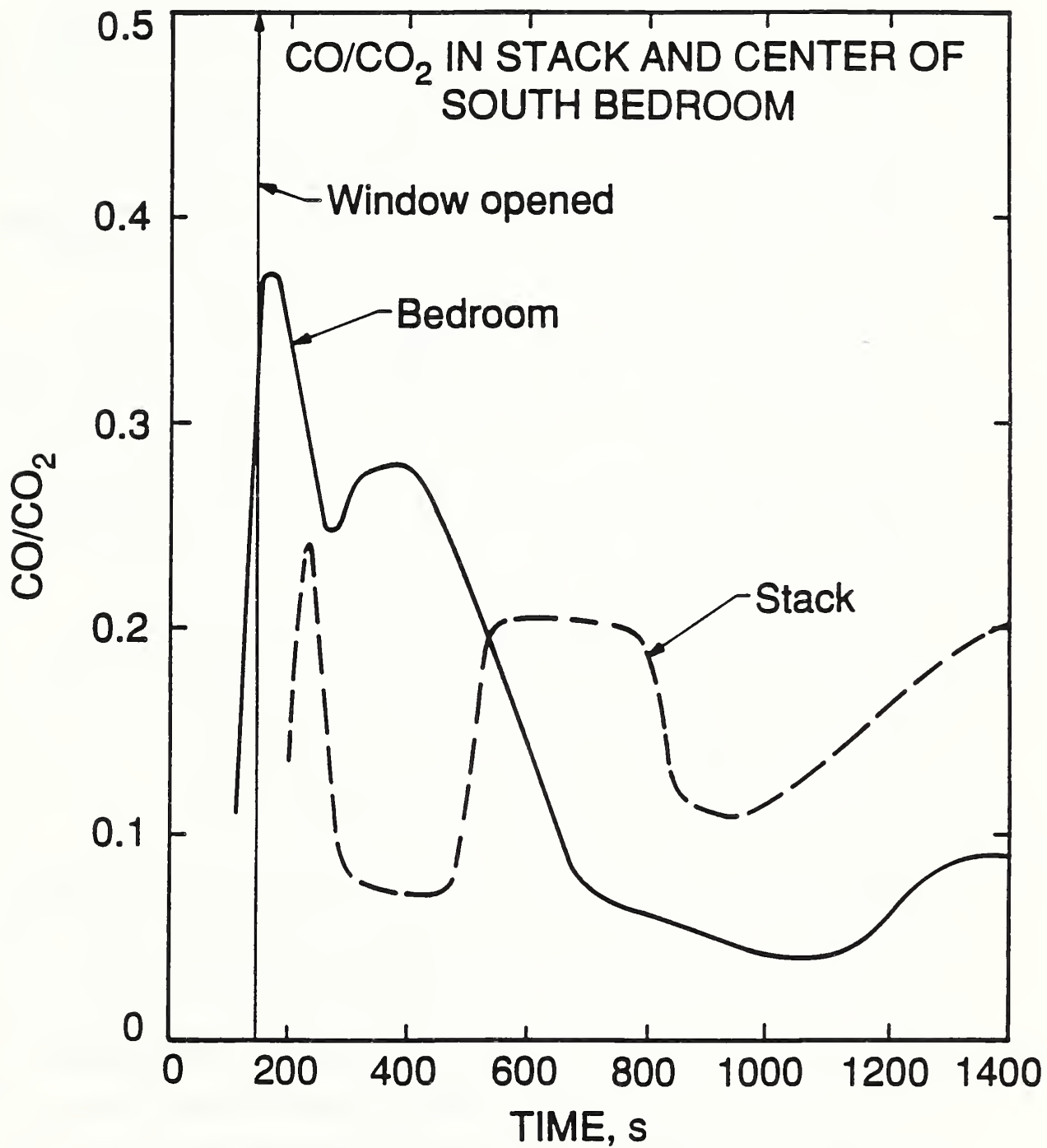
or molar $CO/CO_2 = 0.5$

Figure 10

Figure 11

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SUMMARY OF WORKING GROUP DELIBERATIONS AND RECOMMENDATIONS

Both working groups met for several hours at the end of the first day. The discussions were highly technical and very free-wheeling. A large fraction of these discussions has been tape-recorded and provides a great deal of insight into the problem of CO formation. These discussions will not be detailed here primarily because the chairmen of the two working groups did outstanding jobs of distilling the various comments and viewpoints during their presentations to the workshop on the following day.

The presentations by the chairmen of the two working groups will be discussed utilizing typed copies of the handwritten visuals which were shown. Each presentation was followed by a discussion period. The most important comments and any responses will be summarized as well. Keep in mind that these reports and discussion form the basis for the final recommendations of the workshop which are included in the next section.

During the meeting the presentation order of groups I and II were reversed from that listed in the schedule provided in Appendix B. The findings of group I will be discussed first.

Group I (Fundamentals): Chaired by Professor Faeth

The visuals used by Professor Faeth are shown on the following three pages. Visual I is a list of areas where this working group believes research is required in order to be able to understand the formation of CO in fires and to develop predictive capabilities based on fundamental understanding of the physics and chemistry. The order in which the topics are listed reflects the relative priorities assigned to each subject by the members of the working group.

DEVELOPING A PREDICTIVE CAPABILITY
FOR CO FORMATION IN FLAMES

FUNDAMENTAL ASPECTS

1. DIAGNOSTICS FOR INSTANTANEOUS PROPERTIES OF SOOT-CONTAINING TURBULENT FLOWS.

    (i)   Limitations of laminar flamelet concept.

    (ii) Turbulent chemistry.

2. STRUCTURE OF UNDERVENTILATED FLAMES.

    (i)   Post-flame yields of CO.

    (ii) Non-traditional conditions (in upper layer, vitiated environments, aged pyrolyzed fuels).

    (iii) Stretch and Extinction.

3. STRUCTURE AND CHEMISTRY OF UPPER LAYERS.

    (i)   Reactivity and effects of long residence time.

    (ii) Extent of mixing and stratification.

4. STRUCTURE OF POST-FLASHOVER FLAMES.

    (i)   Non-premixed oxidation of fuel-rich (pyrolyzed) mixtures.

    (ii) Combustion or mixing.

5. PASSIVE MIXING OF A PYROLYZATE.

    (i)   Conditions required.

    (ii) Mixing with ambient gases and with fresh pyrolyzate.

6. REDUCED KINETICS FOR CO CHEMISTRY.

    (i)   More general than global kinetics.

    (ii) Identify critical steps.

Visual I--Group I

WORKING HYPOTHESIS:

(1) Both laminar and turbulent flames are relevant through the laminar flamelet approximation.

(2) Various laminar geometries are relevant.

VIEW OF ISSUES FROM LAMINAR FLAMELET PERSPECTIVE
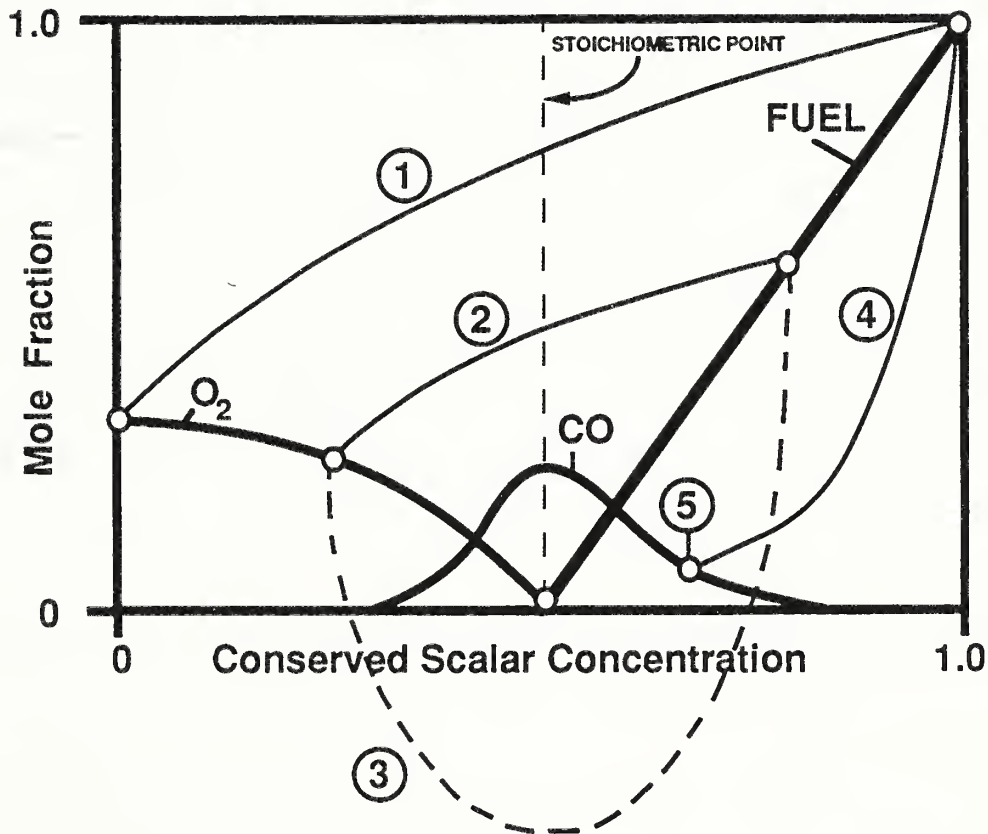
1. Conventional Overventilated Flame.

2. Underventilated Flame (or vitiated environments).

3. Passive Mixing of a Pyrolyzate (Shunting)

4. Mixing with Pyrolyzate Source.

5. Transport-Free Aging of a Pyrolyzate.

Visual II lists two working hypotheses which this working group used as guides in their deliberations. The first reflects the group's belief that the laminar flamelet concept offers an attractive theoretical framework for analyzing CO formation in complex fire situations. For this reason, investigations in both turbulent and laminar flames are valuable. This idea is carried over into the second statement where it is suggested that the laminar flame investigations should be made in several different geometries.

The most crucial need (1, visual I) was judged to be the development of experimental diagnostics which are capable of providing spatially- and temporally-resolved measurements of gas properties and composition within soot-containing turbulent flows. No such diagnostic is currently available. This research area was recognized as being very high-risk due to the complexities involved, but, if successfully completed, to offer the highest payoff with regard to a fundamental understanding of CO formation in complex environments.

The second research area listed (2) was experimental and theoretical studies of underventilated flames. This area was considered to have a slightly lower priority than (1), but to have a greater probability of success within a reasonable time frame. Several topics for investigation are suggested in i-iii listed under (2). It is interesting that the workshop members concurred that the reason these topics have received little research attention up to now is their relative unimportance in many practical combustion systems. On the other hand, these areas are of central importance to the fire problem.

The third research area (3) concerns the possible role of chemistry in the heated upper layers which form in enclosure fires. The regions considered are those outside of the fire plume where combustion is occurring. Both

homogenous (gas phase) and inhomogeneous (e.g., catalytic reactions on soot particles) are included. The working group felt that a more complete understanding of the mixing and stratification within the upper layer would be required.

The fourth research area (4) is based on the conclusion reached during the earlier discussion that very little is known about the possible combustion of upper-layer gases (which may be fuel rich) when they are vented from an enclosure containing a fire into an area with higher O_2 concentration. Subtopics i and ii reflect uncertainties of whether or not these gases will burn further, and, if combustion does occur, its effectiveness in removing CO and other products of incomplete combustion.

Research area (5) is concerned with the conditions for which passive mixing of pyrolyzate is possible. This would be relevant to area (4) above as well as the production of fresh pyrolyzate due to heating of fuel sources within the enclosure, but not within the combusting plume. Pyrolized gases produced in the latter manner could enter the upper layer or vitiate the lower layer.

The last research area (6) concerns the use of kinetic models to predict CO levels where the fire environment is known, and is based on the conclusion that global kinetics models are not appropriate. Full kinetic models have been very successful, but are computationally intensive. Reduced kinetic models offer an opportunity to obtain useful predictions, but with a considerably-reduced computational overhead. Reactions in the presence of soot must also be considered.

Visual III is a diagram based on the laminar flamelet concept which Professor Faeth generated to clarify some of the earlier discussion. This

diagram shows many of the different chemical and mixing pathways which have been identified as being important.

The pathway marked "1" corresponds to overventilated burning and is the normal curve utilized for laminar flamelet calculations. It describes the combustion of fuel by unvitiated air and gives the locus of states within the combustion process as a function of the mixing level--represented by mixture fraction. In this case, if excess air is available so that local fuel equivalence ratios are less than roughly 0.5, emission of CO from the flame is very small based on current information (see the state relationship for methane/air flames on p. 17). However, if entrainment of air is not sufficient to reach these levels, or an individual is exposed to the gas before these levels are reached, significant CO would be encountered.

The pathway marked "2" corresponds to combustion of partially-pyrolyzed fuel in a partially-vitiated environment. It is not known whether or not this type of burning would obey the same state relationship as found for fully-ventilated burning: this is an important research topic. If the behavior is the same, the propensity for emitting CO is increased for this pathway in comparison to pathway 1.

If the combustion is quenched, the vitiated air and pyrolyzed fuel will passively mix. This is called "shunting" and is represented by pathway "3". Since fuel-rich conditions involve significant concentrations of CO, shunting of this type can yield significant emissions of CO. However, conditions required for passive mixing are not understood.

Pathways "4" and "5" involve mixing of pyrolyzate with fresh fuel, or new pyrolyzate, by flow along fuel surfaces, and transport-free aging of a pyrolyzate, respectively. Phenomena of this type have not been studied in

connection with development of the laminar flamelet concept and deserve study as potential mechanisms influencing CO emission from flames.

The workshop members had very little to add to Professor Faeth's lists. Several clarifications were made. The discussion then turned to technical issues of how certain experiments were related to the different research topics which had been suggested. These discussions will not be summarized.

Group II (Engineering): Chaired by Dr. Beyler

The visuals used by Dr. Beyler are included on the following pages. The first (visual I) is a summary of four areas which the working group identified as being important for engineering-based predictions of CO formation in fires. Each of these areas is discussed in more detail on later visuals. It is important to note that this working group did not attempt to prioritize their recommendations, and their order of appearance has no particular importance.

This working group also emphasized the importance of an improved understanding of mass loss rate for CO production. As they note, all CO production predictions are ultimately based on knowledge of fuel volatilization rate. One of their recommendations was that a workshop similar to this one be held on burning rate.

The first research area discussed (visual II) is O_2-limited two-layer burning. This issue is concerned with the behavior of a heated upper layer exiting through a vent and its subsequent combustion behavior. Topic (1) deals with an evaluation of scaling behavior. Comparisons should be made between one meter-scale experiments (planned for VPISU) and full-scale experiments. This comparison will allow an assessment to be made of the appropriateness of utilizing small-scale experiments for investigation of full-scale fire behavior.

PRIORITY RESEARCH AREAS

1. O_2 Limited Two Layer Burning.

2. Open Burning.

3. Fundamentals.

4. Measurement Methods.

RECOMMENDATIONS

Establish a workshop on burning rate and formulate a long range plan.

All CO production predictions are based on a knowledge of fuel volatilization rate.

<u>Visual I--Group II</u>

O_2 LIMITED TWO LAYER BURNING

1. Experimental evaluation of scaling (turbulence).

    One meter versus full scale compartment.

2. Efficiency of external flames in destroying CO.

    Evaluate the effects of:

    Mixing

    Configuration

    Heat loss

    Product recirculation

3. Evaluate the effect of chemical structure of the fuel on the correlation of CO mole fractions in terms of the fuel equivalence ratio.

4. Explore the universality of correlations of chemical species with mixture fraction (or fuel equivalence ratio).

    (e.g., steady and transient two-layer combustion, in flames, etc.)

<u>Visual II--Group II</u>

OPEN BURNING

1. Evaluate the laminar flamelet model for predicting CO mole fraction in open burning.

2. Develop a data base for "real" materials.

       Explore the effects of:

              scale

              configuration

              mixtures of materials

FUNDAMENTALS

1. Determine conditions where CO chemistry is frozen (composition and temperature), including non flaming oxidation and fuel decomposition.

2. Model laminar underventilated diffusion flame combustion using full kinetics to determine mechanism of CO survival. Compare with experiments.

3. Explore CO generation as extinction is approached in vitiated environment, including reducing lowest oxygen index via radiation of solid fuels.

<u>Visual IV--Group II</u>

MEASUREMENT METHODS

1. Evaluate probe effects in CO sampling in reacting flows.

2. Review and evaluate full scale measurement methods.

    Include analysis of the accuracy and reliability of:

    Instrumentation

    Analytical techniques

    Experimental designs (including statistical design of test series)

3. Develop methods for measuring CO generation and fuel equivalence ratio in full scale experiments.

Visual V--Group II

40

The second research topic (2) considers the question of whether or not an external flame destroys CO. Important parameters which should be considered are mixing of the vent "jet" gases with the surroundings, configuration (e.g., whether the vent is a window, a doorway into a long corridor, or a doorway into another room), sources of heat losses, and product gas recirculation.

Topic (3) assumes that an engineering correlation of experimental findings can be obtained by plotting CO concentration in terms of a global fuel equivalence ratio. These correlations must be obtained for different fuels typical of actual fires.

The possible utility of the fuel equivalence ratio correlation is reflected in (4) where it is recommended that the concept be considered for a wide variety of burning conditions. Before this is possible, it is necessary to verify that the concept is valid.

Visual III discusses experiments on fires burning in the open. These measurements are justified by a need to validate the laminar flamelet model for the prediction of CO mass fraction. It is also suggested that a data base of experimental results be collected in order to investigate the effects of scale, configuration, and fuel effects on CO production. There was significant discussion of whether or not these experiments are relevant to CO prediction in enclosure fires. Even though far from a unanimous view, the majority view was that such measurements are warranted by a need to consider baseline cases and test theoretical concepts.

This working group also recommended three areas for investigation which they considered as being of a more fundamental nature. These are included in Visual IV. The first is to consider conditions under which CO chemistry is frozen. The basis for this recommendation is the possibility of upper layer chemistry and nonflaming fuel pyrolysis and oxidation. If these processes are

shown to be unimportant, it will considerably simplify the analysis of CO formation.

The second area is the modeling of underventilated laminar diffusion flames. The goal here is to understand the formation of CO in conditions where underventilated combustion takes place. The working group noted there is some question concerning whether or not the experimental measurements are technically feasible with present technologies.

The final fundamental area recommended (3) is the investigation of CO generation as extinction is approached. The principal interest here are cases where pyrolysis of fuels produces a gas which can then mix with vitiated gases and burn.

This working group also identified measurement methods as being an area requiring attention (see Visual V). There was concern (area 1) that current probing techniques are providing inaccurate measurements for regions where reactions are still occurring. The second area they suggested was the collection of a data base of full-scale measurements which would allow an assessment of the accuracy and reliability of the instrumentation, analytical techniques, and statistical analysis which were employed. The inclusion of this item reflects the group's uneasiness over the quality of past and present measurements. The final area mentioned was the development of new diagnostics which will allow measurements of CO concentrations and local equivalence ratio in full-scale experiments. The motivation here, as in the fundamental case, is to verify that correlations of CO concentrations in terms of fuel equivalence ratio provide a viable engineering means for predictions of CO levels. In this case the principal focus is on global measurements.

FINAL RECOMMENDATIONS OF WORKSHOP PARTICIPANTS

During the final session of the workshop recommendations were generated for areas of research which should be emphasized by the CO priority project. These recommendations were distilled from the working group presentations and represent the research areas which the workshop members believe offer the greatest potential for contributing to an increased ability to predict CO in fires. Both fundamental and engineering viewpoints are represented and in some cases the two approaches overlap.

One point which became clear during this final discussion was the impossibility of isolating CO formation from other problems which are important in fire science and combustion. Two examples which were emphasized were mass loss behavior and turbulent combustion. It was agreed that progress in these areas would be required in order to improve predictive capabilities for CO. Recognizing this reality, the workshop participants provided the following list of observations and recommendations dealing primarily with CO formation. The priority assigned to each is given roughly by the presentation order and reflects the author's interpretation based on discussions during the workshop.

1. Experiments clearly suggest that high concentrations of CO result principally from burning in underventilated conditions. The degree of vitiation appears to be important only when oxygen concentrations are too low to support combustion. Experiments and theoretical efforts are required to understand the formation mechanisms of and to allow prediction of high CO concentrations. Such studies should be assigned the highest priority. Investigations of laminar flames and buoyancy-driven turbulent flames are both necessary.

2. Existing experimental diagnostic techniques do not provide adequate capabilities to answer the questions which must be addressed when CO formation in fires is considered. The lack of suitable diagnostics represents a serious hinderance to the priority project and must be addressed. Inadequacies are apparent in all experiments from the smallest laminar flame to full-scale turbulent fires. Principal problems are the absence of suitable sampling techniques and the presence of soot in fires which acts as an interferant and, at the same time, must also be characterized. Existing diagnostic methods must be improved and more carefully applied and new methods capable of time- and space-resolved concentration and/or temperature measurement in soot-laden flows developed. Particularly important needs are for techniques which allow local and global equivalence ratios to be determined accurately.

3. The observation that CO concentrations can be correlated in terms of the global fuel equivalence ratio provides the most logical starting point for an engineering correlation of CO production within enclosures. Theoretical efforts are necessary to allow the correlation in terms of the global equivalence ratio to be understood in terms of the local combustion environment within the combusting plume. Laminar flamelet theory provides the most logical starting point for these efforts. Experiments are necessary to characterize the conditions for which the global fuel equivalence ratio concept is valid and to verify whether or not it can be extended to developing full-scale fires.

4. The understanding of the combustion behavior of upper layer gases emitted through a vent in an enclosure containing a fire is very poor.

Experiments must be formulated which determine the parameters which control this process and correlations and/or theoretical models must be developed which allow the degree of CO burnout to be estimated as a function of appropriate fire conditions.

5.   The role of "upper-layer chemistry" must be clarified. Conditions (chemical and thermal) where the upper layer continues to react and for which it is passive (with regard to additional CO formation or removal) need to be identified. Full kinetic calculations and reduced mechanisms offer particular promise for this problem. The role of inhomogeneous chemistry must be experimentally investigated and incorporated into kinetic models.

6.   Scaling effects must be investigated. It is recognized that full-scale testing is necessarily limited and that experiments on smaller scales must be devised. This is only possible if scaling effects are characterized.

ACKNOWLEDGEMENTS

The chairman would like to thank all of the participants of the workshop for
their participation. Their efforts made the workshop an enjoyable experience
and a resounding success. Their willingness to convene over a weekend is
"above and beyond" the effort which can be reasonably expected. Special
thanks are due to Sue Riggin who insured that the meeting was organized
efficiently and ran smoothly.

APPENDIX A

Workshop Participants

Workshop Members

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APPENDIX B

Workshop Schedule

Workshop on
DEVELOPING A PREDICTIVE CAPABILITY FOR CO FORMATION IN FIRES
Clearwater, FL

SCHEDULE

Saturday, December 3, 1988

8:30 a.m.: Complementary Continental Breakfast and Informal Discussion

9:00 a.m.: Welcome and Introduction
Dr. William M. Pitts, NIST

Short Reviews:

9:30 a.m.: Professor Houston Miller, George Washington

9:45 a.m.: Professor Robert Santoro, Penn State

10:00 a.m.: Dr. Richard Yetter, Princeton

10:15 a.m.: Dr. Vito Babrauskas, NIST

10:30 a.m.: Professor Gerard Faeth, Michigan

10:45 a.m.: Coffee Break and Discussion

11:15 a.m.: Dr. James Quintiere, speaking for
Professor Edward Zukoski, Cal Tech

11:30 a.m.: Professor Richard Roby, VPISU
Dr. Craig Beyler, FST

11:45 a.m.: Dr. George Mulholland, NIST

Roundtable Discussion:

12:00 p.m.: Discussion Leader: Dr. William M. Pitts

12:45 p.m.: Break for Afternoon

Working Group Meetings:

4:30 p.m.: Group I--Leader: Professor Faeth
Group II--Leader: Dr. Craig Beyler

6:30 p.m.: Break for day

Sunday, December 4, 1988

8:30 a.m.:   Complementary Continental Breakfast and Informal Discussion

9:00 a.m.:   Introductory Remarks
             Dr. William M. Pitts

Group Reports:

9:15 a.m.:   Group I Report

9:45 a.m.:   Discussion of Group I Report

10:15 a.m.: Group II Report

10:45 a.m.: Discussion of Group II Report

11:15 a.m.: Coffee Break and Discussion

Formulate Final Group Recommendations:

11:45 a.m.: Formulate Formal Recommendations

12:45 p.m.: Final Comments

1:00 p.m.:   Adjournment

APPENDIX C

Working Group Members

DEVELOPING A PREDICTIVE CAPABILITY FOR CO FORMATION IN FIRES

WORKING GROUPS

GROUP I

Professor Gerard M. Faeth, Chair

Dr. Richard Gann

Professor J. Houston Miller

Professor Robert J. Santoro

Dr. Rich Yetter

GROUP II

Dr. Craig Beyler, Chair

Dr. Vytenis Babrauskas

Dr. George Mulholland

Dr. James G. Quintiere

Professor Richard J. Roby

Dr. Frederick Williams

APPENDIX D

Instructions for Working Groups

WORKING GROUPS

- Designed to be interactive "brainstorming" sessions

- Groups are constituted to focus on "fundamental" and "engineering" aspects

- Most important phase of workshop

- Make recommendations of which areas require investigation and suggest priority

- Suggest types of experiments required to address these areas, at this point do not consider cost (but not too "pie-in-the-sky")

- Provide written input

- Prepare for group presentations tomorrow

APPENDIX E

List of Research Areas Suggested by Earlier Workshop

RECOMMENDATIONS OF 1985 WORKSHOP

| CO Formation Mechanism	Important?	Need Research?
1) Radiatively quenched eddies	?	yes
2) Quenched plume by ceiling layer	yes	yes
3) Low O_2 Concentration (as in lower layer)	?	< 17% O_2
4) High CO in smoldering	yes	yes
5) Water (sprinklers) on smoldering fuel residue	yes	yes
6) Highly vitiated eddies	?	no
7) Effect of Cl, Br, and other inhibition in gas phase (on CO combustion)	yes	yes
8) Fire out the door in very fuel rich ceiling jet	Yes, very	yes
9) Oxidative pyrolysis of solids	yes	yes

APPENDIX F

Written Summaries of Presentations

Insights on CO Formation Chemistry in Diffusion Flames: Conserved Scalar Correlations and Partial Equilibrium

J. Houston Miller
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Washington, D.C. 20052

In my short talk, I will present data from our structural studies of a laminar methane/air diffusion flame which are relevant to the chemistry of carbon monoxide formation and destruction. I will examine both the correlation of CO concentration with local equivalence ratio and evidence for and against partial equilibrium in the water-gas shift equilibrium. The latter calculation will consider both the overall process:

$$CO + H_2O = H_2 + CO_2 \quad (R1)$$
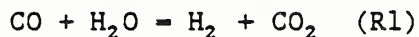
and the component elementary reactions:

$$CO + OH\cdot = H\cdot + CO2 \quad (R2)$$

$$H\cdot + H_2O = H_2 + OH\cdot \quad (R3)$$
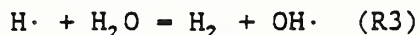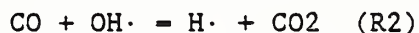
Evidence from the literature and our own work will be presented for equilibrium in R3. Therefore an estimate can be made for the concentration of hydrogen atoms from measured concentrations of H_2O, H_2 and $OH\cdot$. This estimated H-atom profile can then be used to test for equilibrium in R2.

SOOT PARTICLE FORMATION AND DESTRUCTION IN DIFFUSION FLAMES

A Study of the Relationship Between Soot Particle Formation and CO Emission in Laminar Diffusion Flames

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University Park, PA 16802

The formation of CO in fires is an area of active research because of its impact on fire victim fatalities. Although several studies have clearly identified conditions under which CO is observed in the product gases of a fire, a quantitative predictive modeling capability is presently not available for conditions applicable to fire situations. Studies have focused on the effects of turbulent mixing as well as the importance of fuel molecular structure on the emission of CO from fires. Several of these studies have shown that the local equivalence ratio for fuel rich conditions and the tendency of a fuel to soot qualitatively correlate the observed trends. The observations that chemical equilibrium calculations fail to reproduce the measured results has led to consideration of "frozen" chemistry approaches or argue for the need to apply detailed chemical kinetic models.

In studies presently underway at Penn State, the relationship between soot particle formation and CO emission from laminar diffusion flames is being investigated as a possible mechanism for CO production in fires. The motivation for these studies is the recognition that CO and soot oxidation have several similar features. First, in fuel rich regions both are primarily oxidized through reactions with OH radicals and thus compete for the same species. Secondly, the reaction rates for both soot and CO are relatively slow as compared to reactions involving other hydrocarbon species. This feature further argues for a potential competitive route between the two combustion products. In addition to potential chemical kinetic based effects, soot particles are known to enhance radiative transfer in flames, thus effectively lowering the temperature. Lower temperature regions would result in slower chemical kinetic rates and less CO oxidation as well.

The possibility of a synergistic relationship between the formation of soot and CO is not a new idea. Previous workers including Fenimore, Roper, Millikan, Freidman and others have made similar observations. However, in the present studies a systematic study of the evolution of the soot particle field and CO emissions from laminar diffusion flames is being undertaken to provide a quantitative basis from which to examine both chemical kinetic and temperature effects. The initial studies have emphasized the study of the soot formation aspects of the problem. However, recent work is concentrating on examining CO emission in relation to the presence of soot particles. In the workshop presentation, a summary of the background and motivation for the present studies will be given along with a review of the present status of the CO studies.

KINETIC STUDIES OF CO OXIDATION AND INHIBITION

R.A. Yetter
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Princeton, NJ 08544

Abstract

Carbon monoxide is a reaction intermediate formed during the oxidation of all hydrocarbons. A fundamental understanding of CO oxidation and its inhibition and quenching characteristics is therefore important to fire research. These gas-phase kinetic processes have been and continue to be studied in the Fuels Research Laboratory at Princeton University. The current research efforts include:

(i)   kinetic studies (experimental, modeling and sensitivity analysis) of $CO/H_2/O_2$ chemistry,

(ii)   kinetic studies of $CO/H_2/N_2O/NO_2/NO$ chemistry,

(iii)   perturbation studies of $CO/H_2/O_2$ and $CO/H_2/N_2O/NO_2/NO$ chemistry by (a) alkyl compounds, aromatics, alcohols, aldehydes, and (b) chlorinated hydrocarbons, and

(iv)   elementary reaction model reduction and lumping of $CO/H_2/O_2/NO_x$ chemistry.

The objectives, findings, and status of each of these efforts, as related to fire research, will be discussed.

CO prediction in fires – current needs

Vyto Babrauskas/NIST ■ November 29, 1988

Background

- CO is still the main cause of deaths in fires.
- Increased use of plastics has not revealed actual mortalities due to "supertoxicants."
- Toxic potency of combustion products from fires can be predicted adequately, in most cases, if the amounts of CO, CO_2, HCl, HBr, HCN, and low O_2 are known. The prediction will be extremely good once a few additional gases (*e.g.*, HF, acrolein, NO_2, TDI, etc) are added.
- The only *intrinsically* valid fire test is a full-scale, fully-furnished room fire test.
- Due to reasons of cost, routine predictions of fire hazard and fire mortality must be based on bench-scale data.
- To predict the actual amount of a toxic species x being emitted in full scale, it is necessary to know the mass burning rate of the fuel, and multiply that by the yield of species x.
- Ability to predict yields[1] of CO_2, HCl, HBr, HCN, etc., in full-scale, fully-furnished room fires is good, based on bench-scale test results.
- Recent research has shown that not only are bench-scale tests unable to show similar CO yields as do the fully-furnished, full-scale room fires, but even full-scale furniture calorimeter (■ open burning) tests do not give the correct CO yield.
- Our ability to predict full-scale mass burning rates for real combustibles is extremely limited, *e.g.*, Wickström's correlations for wall linings and Babrauskas' correlations for upholstered furniture.
- Therefore, currently much of the power of advanced fire models cannot be reliably put to use.

CO production – a conceptual framework

- CO yields in full-scale room fires appear to be little-influenced by the nature of the fuel being burned.
- In the early stages of fire growth in a room, CO yield appears to be primarily related to ϕ (actual fuel/air ratio, divided by the stoichiometric fuel/air ratio). There is a possibility that there is a universal curve relating CO yield to ϕ over most of the range of ϕ. There is presumed to be some fuel-type dependence at the $\phi \rightarrow 0$ asymptote, however.
- As the fire progresses, the fuel/air ratio will keep increasing and, therefore, the CO yield will rise.
- In the later stages of fire growth, there will be a fire plume formed at the door/window. The bulk of the combustion products being delivered to the occupants will be the outflow of that door plume. Some occupants, however, may be exposed to upper layer hot gases which flow out through cracks, or otherwise do not pass through the door plume. The CO concentrations in the stream which did not pass through the door plume will be, of course, different from the one that did.

---

[1] yield of species x = (kg x produced)/(kg specimen mass lost)

- The door plume may be effective, semi-effective, or ineffective in incinerating the CO coming from the fire room. If the plume is effectively incinerating, then very low values of CO yield may be achieved. This explains results where the CO yield is less post-flashover than pre-flashover, or when CO becomes less for a room with more fuel loading in it.
- It may be surmised that the plume is effective when it goes straight up, does not impinge on any physical obstacles, and if it is located in a plentiful oxygen area. Conversely, effectiveness may be low if the plume is flattened horizontally against a ceiling, impinges on obstacles which are heat drains, or gets its air by pulling from a long corridor rather than from the open atmosphere.

Research needed

I. Full-scale CO yields

    A. Determine if there is a largely universal CO yield *vs* ϕ curve. It is possible that this could be done in reduced scale (say, 1 m box) tests, if it can be determined that the scale of turbulence is not important. The basic test series could start out with gas burners of various fuels, driving the room to ever-increasing ϕ values. If the results show that universality is not achieved, then, of course, an account of fuel type would have made.

    B. Determine the geometric condition details leading to effective, semi-effective, or ineffective plume incineration. Again, this could conceivably be done in reduced scale.

    C. Quantify the actual CO yields for effective and semi-effective plume incineration conditions (for ineffective plumes, the yield would, by definition, be the same as within the room itself, based on the ϕ curve).

II. Full-scale mass loss rates

    A. Wall + ceiling fires. A method for heat release rate (by Wickström) has been developed. Presumably it would not be difficult to adapt it for mass loss rate, but this still needs to be done.

    B. Wall (alone) fires. A method does not yet exist, although Magnusson has had a number of tests run at Statens Provningsanstalt for these conditions.

    C. Ceiling fires. No data or method yet.

    D. Floor fires. No data or method yet.

    E. Upholstered furniture fires. A method for heat release rate (by Babrauskas) is available. This would need to be moved over to the mass loss rate variable.

    F. Mattress fires. Only some very old correlations on hand. Should be re-done.

    G. Case goods. No data or method yet.

CARBON MONOXIDE FORMATION IN FLAMES: A Laminar Flamelet Perspective

G.M. FAETH
Arthur B. Modine Professor
of Aerospace Engineering
Department of Aerospace Engineering
UNIVERSITY OF MICHIGAN
Ann Arbor, Michigan

The laminar flamelet concept has proven to be valuable for estimating the structure of turbulent flames. The concept is based on the fact that the concentrations of major gas species and temperatures are primarily functions of mixture fraction (or correspondingly fuel-equivalence ratio) in laminar diffusion flames -- called state relationships. The laminar flamelet concept implies that the same state relationships (for a particular reactant combination and ambient conditions) apply in turbulent flames, assuming that the turbulent flames correspond to wrinkled laminar flames.

When reaction rates are fast, and the exchange coefficients of all species and heat are nearly equal, the laminar flamelet concept is justified by lack of differential diffusion effects and the capability of the flame to maintain local thermodynamic equilibrium. In fact, good state relationship correlations, approaching thermodynamic equilibrium, have been observed for carbon monoxide/air flames of reasonable size. State relationships also approximate thermodynamic equilibrium for lean conditions in hydrocarbon/air flames, satisfying the laminar flamelet concept. Reasonably good state relationship correlations have also been observed for rich conditions in laminar hydrocarbon/air flames: these correlations depart from thermodynamic equilibrium due to the slow chemistry of fuel decomposition and soot processes but the departures are relatively universal. However, the laminar flamelet concept is not valid everywhere in flames: it breaks down in regions of flame attachment and in regions of rapid turbulent mixing (approaching quenching limits) where the wrinkled laminar flame character is lost. Furthermore, consideration of state relationships has been undertaken primarily to characterize concentrations of major gas species for evaluation of mixing properties and flame radiation: use of the concept for small quantities of toxic materials has never been advocated or studied in any depth. Recent work in this laboratory, however, has shown that soot emissions can be usefully interpreted in terms of the laminar flamelet concept for large flames having sufficiently long residence times.

Recognizing the limitations, study of the state relationships for carbon monoxide/air and hydrocarbon/air flames shows that concentrations of carbon monoxide become small for fuel-equivalence ratios less than 0.5, more or less corresponding to equilibrium predications. This suggests that dangerous levels of carbon monoxide in fires result form incomplete mixing, with additional contributions from regions of high scalar dissipation rates where quenching limits are approached. However, effects of vitiated ambient gases, and long residence times at intermediate mixing levels have not been studied, and could modify carbon monoxide concentrations from levels expected from the laminar flamelet concept.

The main contribution of the laminar flamelet concept to practical turbulent flames is that it connects results for laminar flames, which are easier to study, to turbulent flames. The concept also provides a means of separating effects of mixing from other phenomena -- like finite rate chemistry. Thus, the laminar flamelet concept provides a useful perspective for studying carbon monoxide formation in flames which should be exploited during the study being considered by NIST.

CARBON MONOXIDE PRODUCTION IN TWO–LAYERED NATURAL GAS FIRES

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ABSTRACT

A fire burning in an enclosure with restricted ventilation will cause the accumulation of a layer of warm products of combustion mixed with entrained air adjacent to the ceiling. Given a sufficient supply of fuel, the depth of this layer will extend to occupy a significant fraction of the volume of the room. Eventually, the interface between this vitiated ceiling layer and the uncontaminated environment below will position itself so that a large portion of the combustion processes occur in this vitiated layer. Recent experimental work described here has been concerned with the development of accurate descriptions of entrainment and carbon monoxide production rates in the plume of a turbulent methane diffusion flame burning in this two–layered configuration. The enclosure was modeled by placing a hood above a burner so that it accumulated the plume gases. Measurements of the composition of these gases allowed the computation of stoichiometries and air entrainment rates. These investigations showed that the concentration of carbon monoxide present in the ceiling layer depended only on the stoichiometry of the gases present in this layer and was independent of the fuel–air ratio of the mass transported into the layer by the plume. When the product layer equivalence ratio was below 0.5, no measurable amounts of carbon monoxide were detected. For conditions in the ceiling layer with equivalence ratios from 0.5 to 1.5, the concentration of carbon monoxide increased nearly linearly to a level of almost 2% and remained fixed for more fuel-rich conditions. In contrast, when the fire was burning in a single vitiated layer, no measurable amounts of carbon monoxide were found for conditions up to the extinction limit.

"DEFINING CONDITIONS WHERE CO DOMINATES THE TOXIC HAZARD"

Dr. Craig Beyler
Fire Science Technologies
Cincinnati OH 45251

The prediction of CO in fire is important solely due to the potential for human exposure to this toxic gas. Given the goal of reducing the fire deaths due to toxic gas exposure, it is important for us to identify those fire conditions under which CO represents the dominant toxicant. This will guide us in establishing priorities in CO formation research.

Dr. Beyler will review his recent work in the comparison of the hazards due to elevated temperatures, oxygen depletion, and carbon monoxide under smoldering, "open burning", and oxygen limited two layer combustion conditions. The results of this analysis indicate that CO is most important in oxygen limited two layer combustion conditions and in smoldering combustion conditions. For most materials burning in the "open burning" mode, thermal effects and oxygen depletion dominate over CO.

"METHODS FOR INVESTIGATING CO FORMATION IN COMPARTMENT FIRES"

Prof. Richard Roby
Dept. of Mechanical Engineering
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Developing predictive capabilities for CO formation in two layer compartment fire environments is in its early stages of development. To date fuels examined have not, for the most, part been materials of importance in buildings. The sparsity of data for common polymeric fuels is largely the result of the difficulties inherent in the measurement of the relevant compartment fire variables for "real" materials and realistic compartment fire conditions. Current progress is limited by our ability to conduct well controlled and instrumented compartment fires, which can be designed, probed, and explored to unlock critical data and deduce the physical/chemical processes controlling CO formation.

Dr. Roby will discuss our current state of knowledge of CO formation in two layer compartment fire conditions. He will describe concepts developed for studying toxic gas formation in a two layer compartment fire environment, and progress in their implementation in the current investigation. This discussion will include the design and construction of the combustion apparatus, as well as the physical and chemical measurement systems. Research strategies utilizing this system will be outlined.

CO PRODUCTION DURING FIRE RECONSTRUCTION OF SHARON, PA FIRE

George W. Mulholland
Center for Fire Research

Three mildly retarded women died in their upstairs bedrooms as a result of a fire in a Mercer County Association for the Retarded group home in Sharon, PA. The fire occurred in a plywood lined kitchen in a two-story brick duplex. The generation of CO, low oxygen, and high temperature are all thought to have played a role in this tragic fire.

To provide a better understanding of why the victims died, a full scale fire reconstruction was carried out using a similar but smaller dwelling geometry. This study was led by Mr. B. Nelson, Dr. R. Levine, and Dr. J. Quintiere at the Center for Fire Research. The fuel load consisted of an array of 18 wood cribs, weighing a total of 75 kg, with plywood sheets, weighing 109 kg, located between the rows of cribs. This design was a compromise between simulating the kitchen furniture and wood paneling in the duplex and the need to locate the entire fuel assembly on a load cell. It was estimated that this amount of wood would insure a ventilation controlled burn for the case of an open door and window in the burn room.

At the start of the burn, the kitchen door was open. The fire was ignited using 2 liters of heptane in narrow troughs located under the cribs. The fire intensity grew rapidly approaching flashover conditions at 130 seconds, at which time the kitchen "window" was opened simulating the window breaking in the actual fire. The peak mass loss rate was 0.32 kg/s occurred 160 seconds after ignition after which there was a steady decrease to 0.17 kg/s at 600 seconds. For a well ventilated wood burn, a mass loss of 0.32 kg/s would correspond to a heat release rate of about 3.2 MW; however, the low oxygen concentration measured in the gases leaving the room indicates that the burn was ventilation limited as was planned.

Leaving the kitchen, the combustion gases moved down a hallway, up the stairs, and then into either the south bedroom, which has a window opened 0.15 meters, or the north bedroom. The CO concentration reached a value of 1% at 130 seconds, at which time CO_2 was 4%, the O2 concentration was 16%, and the upper layer temperature was 75°C. By 200 seconds, the CO concentration had increased to 4%, the oxygen concentration had decreased to 8%, and the upper layer temperature had increased to 120°C. This is an untenable condition even for a short time.

The molar ratio of CO to CO_2 concentration is a useful measure of the relative toxicity of the product gases. The peak value of this ratio was 0.37 in the south bedroom at 160 seconds, then decreased to a plateau value of 0.28 before abruptly decreasing at a time of about 420 seconds. The average value of CO/CO_2 over the interval from 160 to 420 was 0.29. A similar trend was observed in the north bedroom but with a higher peak of 0.50 and a mean value of 0.35 over the period from 160 to 420 seconds. The peak values observed in this test are similar to the peak values obtained by Budnick et al.[1,2] in

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[1] Budnick, E.K., "Mobile Home Living Room Fire Studies: The Role of Interior Finish," NBSIR 78-1530.

mobile home living room (CO/CO_2 = 0.46 and 0.63) and bedroom fire studies (CO/CO_2 = 0.51 and 0.40), for which flashover occurred. In both cases the wall paneling and ceiling material were wood and the fires were extinguished at the time of flashover.

These values for the molar ratio CO/CO_2 are to be compared with a value of 0.28 obtained by Beyler[3] for the burning of Ponderosa pine cribs, each of the three to five layers was made up of three, 0.038 m thick, 0.2 m long sticks. The height of the collection hood above the crib was such that the global equivalence ratio was about 1.4. While the peak values are greater than the results of Beyler, the average values are in fair agreement.

The CO/CO_2 ratio of the combustion products coming out of window and going into the exhaust stack was observed to have an initial peak of 0.26 when the window was first opened and then decreased to a value of 0.05 to 0.1 during the period of high CO concentration in the bedrooms. Presumably, a large fraction of the CO was converted to CO_2 as it left the window and continued burning as it mixed with fresh air in the stack. This process can not take place within the structure, because there is no source of fresh air.

One noteworthy feature observed with three CO meters positioned at various location in the test structure was a sudden decrease in the CO concentration at a time of about 450 seconds. There was no corresponding decrease in the CO_2 concentration, in fact, the CO_2 concentration did not reach a peak value of 19% until about 650 seconds and was still 16% at 1100 seconds. There was no indication of a change in the fire character at 450 seconds to suggest a big change in the CO production. Apparently, a slight drop in the mass loss rate changed the fire from slightly fuel rich to slightly fuel lean resulting in an abrupt decrease in the CO production. The fire continued to burn outside the window until about 700 seconds, at which time the flames moved back into the room.

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[2] Budnick, E.K., Klein, D.P., O'Laughlin, R.J., "Mobile Home Bedroom Fire Studies: The Role of Interior Finish," NBSIR78-1531.

[3] Beyler, C.L., "Major Species Production by Solid Fuels in a Two Layer Compartment Fire Environment," Proceedings of First International Symposium on Fire Safety Science, C. Grant and P. Pagni eds., Hemisphere Pub., New York, 431-440, 1986.

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☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

The proceedings and recommendations of a workshop entitled "Workshop on
Developing a Predictive Capability for CO Formation in Fires" are summarized.
This meeting took place on December 3-4, 1988 in Clearwater, Florida. Several
brief technical presentations are critiqued. Short summaries for each talk
are included in an appendix. Findings of two working groups constituted to
address the fundamental and engineering aspects of the workshop topic are
discussed. The most important areas of research required to fulfill the
workshop topic are provided as final recommendations. Six specific areas are
listed. Many workshop details are included in appendices.

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